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Anionic polymerization of a series of 5-membered cyclocarbosiloxanes

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ANIONIC POLYMERIZATION OF A SERIES OF 5-MEMBERED CYCLOCARBOSILOXANES

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ABSTRACT

A study has been made on the anionic polymerization of a series of 5-membered cyclocarbosiloxanes with methyl and/or phenyl substituents. The polymerization was initiated by lithium n-butyldiphenylsilanolate in the presence of tetrahydrofuran. Six 5-membered cyclocarbosiloxanes (2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane; 2,2,5-trimethyl-5-phenyl-1-oxa-2,5-disilacyclopentane; 2,5-dimethyl-2,5-diphenyl-1-oxa-2,5-disilacyclopentane; 2,2-dimethyl-5,5-diphenyl-1-oxa-2,5-disilacyclopentane; 2-methyl-2,5,5-triphenyl-1-oxa-2,5-disilacyclopentane; 2,2,5,5-tetraphenyl-1-oxa-2,5-disilacyclopentane) were synthesized. Since the chemical shifts of the protons of the cyclic monomers and the polymers formed were different, the rate of polymerization of the cyclic monomers was measured utilizing an NMR spectrometer. The effects of tetrahydrofuran concentration, initiator concentration and water concentration on the rate of polymer formation and on the molecular weight of the polymer formed are reported for a cyclocarbosiloxane 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane. Both monomodal and bimodal distributions of molecular weights were obtained on the polymers depending on the relative concentrations of initiator and water. The formation of this type of molecular weight distribution is explained. The rate of polymerization of phenyl substituted cyclocarbosiloxanes is also reported. This study shows that the structure of the growing chain end is important in determining the rate of polymerization. The apparent activation energy of polymerization for the cyclocarbosiloxanes studied was found to be in the range 10 - 14 kcal/mole.

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I. INTRODUCTION

Polyorganosiloxanes have been known since the 1940's and are widely used as fluids, greases, elastomers etc. Many of the polyorganosiloxanes are prepared by the base-catalyzed ring-opening polymerization of cyclosiloxanes. Polyorganosiloxanes prepared by strong base-catalyzed reactions are polydispersed because of equilibration reactions. Since 1969 weak bases such as lithium salts have been used in conjunction with Lewis bases for the ring-opening polymerization of strained cyclosiloxanes. The use of weak bases eliminated the equilibration reactions so that essentially monodispersed polymers have been prepared. Further, the use of lithium bases offered a synthetic route for the preparation of true siloxane block copolymers.

The purpose of this work was to study the anionic polymerization of strained 5-membered cyclocarbosiloxanes. A series of 5-membered cyclocarbosiloxanes with methyl and/or phenyl substituents were synthesized and their polymerization behavior was studied in the presence of lithium n-butyldiphenylsilanolate as the initiator and tetrahydrofuran as the promoter. The rate of polymerization was studied utilizing nuclear magnetic resonance spectrometry. The effects of tetrahydrofuran concentration, initiator concentration and the water concentration on the rate of polymerization and on the molecular weight of the polymer formed, were investigated on a particular cyclocarbosiloxane, 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane. The effects of substituting phenyl for methyl groups and the reaction temperature on the rate of polymer formation were investigated. Detailed study

on the polymerization behavior of the 5-membered cyclocarbosiloxanes has not appeared in the literature.

This work is an intermediate but integral part of the goals of USPH grant-5-Rol-HL-13999-02, which included the synthesis of modified silicone polymers. The polymers reported in this dissertation will be crosslinked to form elastomers which will be tested for biocompatability and subsequent applications in prosthetic devices.

II. REVIEW OF THE LITERATURE

A. SYNTHESIS OF CYCLOSILOXANES

The discovery, isolation and characterization of the first organocyclosiloxanes were accomplished by Kipping[1]. Initially, Kipping was searching for ketonic analogues in diorgano-substituted silicon compounds, but his research led him to the conclusion that the materials he had isolated as silico-ketones ("silicones") were, in fact, silicoethers or siloxanes. Further he identified some of these as closed-ring cyclics composed of alternating silicon and oxygen atoms viz, octaphenylcyclotetrasiloxane[2].

Hyde and Delong[3] isolated hexamethylcyclotrisiloxane in an impure state, along with linear polymeric materials during the hydrolysis of dimethyldichlorosilane. The first comprehensive study on the preparation and properties of a series of purified dimethylcyclosiloxanes was conducted by Hunter et al.[4]. They prepared dimethylcyclosiloxanes of the formula $[(CH_3)_2SiO]_x$, where x was 3 to 8 inclusive, by the pyrolysis of polydimethylsiloxane fluid in the presence of sodium hydroxide. They isolated each member of the series, studied its physical properties and established the structure of these cyclic compounds by chemical analysis and molecular weights, as well as by the regularities in the relationships of their physical properties. Frevel and Hunter[5] also studied the structure of these cyclosiloxanes by means of x-ray diffraction analyses and found that in all cyclosiloxanes except hexamethylcyclotrisiloxane, the ring was puckered. Hexamethylcyclotrisiloxane was found to possess a planar structure similar to that in bentonite. The dimethylcyclosiloxanes $[(CH_3)_2SiO]_x$ where x = 3 to 25 have been identified by Brown and

Slusarczuk[6] by means of chromatographic methods. However, only the lower homologues (x = 3-7) are primary intermediates for polymerization and consequently well known. Piccoli et al.[7] determined the strain energy of hexamethylcyclotrisiloxane by calorimetry to be 3-4 kcal/mol.

B. SYNTHESIS OF CYCLOCARBOSILOXANES

Similar to the cyclosiloxanes is a group of cyclic compounds called cyclocarbosiloxanes containing a Si-C as well as a Si-O ring portion. A comprehensive review has been published[8] recently on the methods of synthesis of several cyclocarbosiloxanes. Some of the important methods for the synthesis of 5, 6, and 7-membered cyclocarbosiloxanes are reviewed here since the higher homologues in these cyclic compounds have not been identified unequivocally.

Kumada and Habuchi[9] described the preparation of the 6-membered cyclocarbosiloxane $(CH_3)_2\overline{SiCH_2CH_2CH_2Si(CH_3)_2O}$ by the hydrolysis of bridge type compounds $Cl(CH_3)_2SiCH_2CH_2CH_2Si(CH_3)_2Cl$. Sommer and Ansul[10] reported the synthesis of the 7-membered cyclocarbosiloxane $(CH_3)_2\overline{Si(CH_2)_4Si(CH_3)_2O}$, by the hydrolysis of 2,7-dimethyl-2,7-difluoro-2,7-disilaoctane, and subsequent dehydration of the dihydroxy compound in the presence of trifluoroacetic acid. Piccoli[7] et al. described the synthesis of the 5-membered cyclocarbosiloxanes of the type $R_1R_2\overline{Si(CH_2)_2R_3R_4SiO}$ where R_1, R_2, R_3 and R_4 = methyl and/or phenyl, by means of the following reactions.

$$ClSi(R_1)(R_2)H + CH_2{=}CHSi(R_3)(R_4)Cl \xrightarrow{H_2PtCl_6\cdot 6H_2O}$$

$$ClSi(R_1)(R_2)CH_2CH_2(R_3)(R_4)SiCl$$

$$ClSi(R_1)(R_2)CH_2CH_2(R_3)(R_4)SiCl \xrightarrow{H_2O} \text{hydrolysate} \xrightarrow[\triangle]{\text{alkali}} \overbrace{Si(R_1)(R_2)CH_2CH_2(R_3)(R_4)SiO}$$

They also estimated the ring strain energy of these cyclocarbosiloxanes to be about 8-12 kcal/mol, by calorimetric measurements, indicating these rings are highly strained. Steward and Sommer[11] prepared $(CH_3)_2\overbrace{SiCH_2C(R)(R')CH_2(CH_3)_2SiO}$, the C-substituted cyclocarbosiloxanes by the hydrolysis of the bridge-type compound with a substituted carbon atom, $ClSi(CH_3)_2C(R)(R')CH_2Si(CH_3)_2Cl$. Weyenberg and Toparcer[12] found that if there was a cyclic group like cyclohexene between the silicon atoms, the cyclization process took place with low yields (20%). Pao-Jen[13] et al. reported that the hydrolytic condensation of these bridge type compounds with more than two hydrolysable groups on the silicon atom led, as a rule, to polycyclic cyclocarbosiloxanes and other cyclocarbosiloxanes with cage-like structures.

Cyclocarbosiloxane with a p-phenylene bridge was obtained by Merker and Scott[14] by the hydrolysis of p-bis(dimethylhydrogensilyl)-benzene in aqueous ethanol and KOH and subsequent thermal cracking of the polymer formed in the presence of lithium hydroxide. The cyclocarbosiloxane obtained was a mixture of dimer and trimer with the structure $[(CH_3)_2Si\text{-}p\text{-}C_6H_4\text{-}Si(CH_3)_2O]_{2 \text{ and } 3}$. The yield reported was 10-30%. The reaction scheme was represented as follows:

$$Br\text{-}C_6H_4\text{-}Br + 2Mg + 2(Me)_2SiHCl \xrightarrow{THF} \begin{matrix} (Me)_2\text{-}Si\text{-}H \\ | \\ C_6H_4 \\ | \\ (Me)_2\text{-}Si\text{-}H \end{matrix} \quad (I)$$

$$+ 2MgClBr \qquad \text{p-Bis(dimethylhydrogensilyl)benzene}$$

$$(I) + EtOH/H_2O \xrightarrow[-H_2]{KOH} \left[-\underset{Me}{\overset{Me}{Si}}-C_6H_4-\underset{Me}{\overset{Me}{Si}}-O- \right]_n$$

$$\bar{M}_n = 2,200$$

(II)

$$(II) \xrightarrow[\triangle]{LiOH} \left[(Me)_2Si\text{-}p\text{-}C_6H_4\text{-}Si(Me)_2O\right]_{2 \text{ and } 3}$$

Andrianov[15] synthesized a number of 6-membered cyclocarbosiloxanes by reacting symmetrical bis(chloromethyl)tetramethyldisiloxane and (alkyl)(aryl)dichlorosilanes with metallic sodium as shown below.

$$ClCH_2Si(Me)_2OSi(Me)_2CH_2Cl + (R)(R')SiCl_2 + 4Na \xrightarrow[\text{toluene}]{\triangle}$$

$$(Me)_2\overline{SiCH_2(R)(R')CH_2Si(Me)_2O} \quad (20\text{-}30\%)$$

Sommer[16] et al. utilized the malonic ester synthesis to synthesize the cyclic diester 1,1-dicarbethoxy-2,2,5,5-tetramethyl-3,5-disila-4-oxacyclohexane by reacting sym-bis(chloromethyl)tetramethyldisiloxane with sodiomalonic ester.

$$ClCH_2Si(Me)_2OSi(Me)_2CH_2Cl + 2\overset{(-)}{C}H(COOEt)_2 \xrightarrow{-2Cl^{(-)}}$$

$$(Me)_2\overline{SiCH_2C(COOEt)_2CH_2Si(Me)_2O} + CH_2(COOEt)_2$$

Simmler[17] et al. similarly prepared the cyano-substituted 6-membered cyclocarbosiloxane by cyanoacetic ester synthesis. Polyakova et al.[18] have prepared a series of 5-membered cyclocarbosiloxanes with different substituents at the carbon atom, by means of cycloaddition reaction between substituted acetylenes and dihydrodisiloxanes in the presence of chloroplatinic acid as the catalyst. The yield of the cyclocarbosiloxane varied between 5 to 75% depending on the structure of the

initial reagents and the reaction conditions.

$$XC\equiv CX' + H(R)(Me)SiOSi(Me)(R)H \xrightarrow[H_2PtCl_6\cdot 6H_2O]{110\text{-}120^{o}}$$

$$(Me)(R)\overline{SiCH(X)CH(X')Si(Me)(R)O}$$

$X = H, C_6H_5$ or C_4H_9

$X' = H, CH_3$ or C_6H_5

and $R = CH_3$ C_2H_5, or C_6H_5

Bulkier substituents on either reactant give lower yields.

C. POLYMERIZATION OF CYCLOSILOXANES

The conversion of low molecular weight cyclosiloxanes and cyclocarbosiloxanes to high polymers involves chemical activation to effect a ring-opening followed by a multistep addition and equilibration. Both bases and acids have been utilized as catalysts for the ring-opening polymerization. These will be reviewed separately.

1. Base-Catalyzed Polymerizations

Hyde[19] disclosed that certain alkali metal hydroxides such as sodium hydroxide and potassium hydroxide, reacted with organocyclosiloxanes to form high polymers. Hurd[20] et al. investigated the polymerization of octamethylcyclotetrasiloxane with various bases. They found qualitatively that the order of reactivity of alkali metal hydroxides toward octamethylcyclotetrasiloxane was CsOH > RbOH > KOH > NaOH > LiOH. The reactivity order was rationalized by them on the basis of an ionic equilibrium.

$$Si(Me)_2OM \rightleftharpoons -Si(Me)_2O^{(-)} + M^{(+)}$$

M = alkali metal

The enhanced reactivity observed in going from Li^+ to Cs^+ was attributed to increased ionization of the metal silanolate to produce the active anionic species.

Kantor et al.[21] investigated the reactivity of dimethylsiloxanes in both cyclic and linear forms to bases such as tetramethylammonium-hydroxide. They established the following reactivity series of low molecular weight siloxane compounds toward bases:

$D_3 > D_4 > MD_2M > MDM > MM$ where D = $(CH_3)_2SiO$ and M = $(CH_3)_3SiO_{1/2}$

Thus hexamethylcyclotrisiloxane (D_3) was found to be more active than octamethylcyclotetrasiloxane (D_4). The least reactive in the series was hexamethyldisiloxane [MM which is $(CH_3)_3SiOSi(CH_3)_3$]. They attributed the greater reactivity of D units to electron withdrawal from silicon by two adjacent oxygens rather than one.

Grubb and Osthoff[22] conducted a detailed kinetic study on the polymerization of octamethylcyclotetrasiloxane (D_4) catalyzed by potassium hydroxide or potassium silanolate. They followed the extent of the reaction by monitoring the vapor pressure of the monomer above the polymerizing system. They found the overall rate of polymerization was first order with respect to monomer concentration and half order with respect to catalyst concentration. Further the overall rate of polymerization was the same whether potassium hydroxide or potassium silanolate was used as the catalyst. These observations led them to propose the following ionic mechanism for the polymerization of cyclic tetramer

(1) $KOH + \left[(Me)_2 SiO\right]_4 \longrightarrow HO\left[(Me)_2SiO\right]_3 -\overset{Me}{\underset{Me}{\overset{|}{\underset{|}{Si}}}}OK$

$$HO\left[(Me_2SiO\right]_3 -\overset{Me}{\underset{Me}{\overset{|}{\underset{|}{Si}}}}OK \overset{k_i}{\rightleftharpoons} HO\left[(Me)_2SiO\right]_3 -\overset{Me}{\underset{Me}{\overset{|}{\underset{|}{Si}}}}O^{(-)} + K^{(+)}$$

(2) $$HO\left[(Me)_2SiO\right]_x -\overset{Me}{\underset{Me}{\overset{|}{\underset{|}{Si}}}}O^{(-)+K^{(+)}} + \left[(Me)_2SiO\right]_4 \underset{k_d}{\overset{k_p}{\rightleftharpoons}}$$

$$HO\left[(Me)_2SiO\right]_{x+4} -\overset{Me}{\underset{Me}{\overset{|}{\underset{|}{Si}}}}O^{(-)} + K^{(+)}$$

(3) $$HO\left[(Me)_2SiO\right]_x -\overset{Me}{\underset{Me}{\overset{|}{\underset{|}{Si}}}}O^{(-)} + K^{(+)} \underset{k_i}{\overset{k_t}{\rightleftharpoons}} HO\ (Me)_2SiO\ K_x$$

The rate controlling step in this scheme was the attack of an ionized species on cyclic tetramer (Step 2). Since the concentration of the ionic species is determined by Step 1, the ionization constant plays an important part. Thus for Step 1

$$K_e = \frac{\left[\equiv SiO^{(-)}\right]\ K^{(+)}}{\left[\equiv SiOK\right]} = \frac{\left[\equiv SiO^{(-)}\right]^2}{\left[\equiv SiOK\right]} = \frac{\left[\equiv SiO^{(-)}\right]^2}{\left[KOH\right]_{added}}$$

$$\left[\equiv SiO^{(-)}\right] = K_e^{\frac{1}{2}}\ KOH^{\frac{1}{2}}_{added}$$

The overall rate of polymerization $k_p = [\equiv Si\text{-}O^{(-)}]\ [Monomer]$

or $k_p \propto Ke^{\frac{1}{2}}[KOH]^{\frac{1}{2}}_{added} \cdot [Monomer]$

Grubb and Osthoff[21] pointed out that any factor which increased the ionization constant should increase the overall rate of polymerization. Their postulates were later verifeid by other workers.[23,24]

The extent of polymerization of these cyclicsiloxanes has been followed by several different methods. Grubb and Osthoff[22] utilized the conventional quenching and weighing method for determining the amount of polymer formed. They also measured the vapor pressure of the monomer during polymerization and determined the amount of monomer that reacted. Ostrozynski[25] utilized gas-liquid chromatography (GLC) as an analytical tool for the determination of the amount of monomer that disappeared. Andrianov[26] followed the course of polymerization of cis-trimethyltriphenylcyclotrisiloxane by means of proton magnetic resonance spectra. The polymerization rate was found in terms of the change in the integral intensities of the methyl-group protons of the monomer and the polymer.

Polydimethylsioloxanes formed by strong base-catalyzed ring-opening polymerizations are usually called equilibrium polymers because the catalyst not only polymerizes but also depolymerizes until the system reaches an equilibrium, and the process is referred to as equilibration. Also because of equilibration, polydimethylsiloxanes are polydispersed.

2. Effects of Media on Base-Catalyzed Polymerization of Cyclosiloxanes

Grubb and Osthoff's mechanism for the polymerization of octamethylcyclotetrasiloxane depicted the silanolate anion as the active intermediate, and pointed out that any factor which increased the ionization constant should increase the overall rate of polymerization. The effect of solvent media on the base-catalyzed polymerization has been studied by several workers. Morton and co-workers[24] found that as the dielectric constant of the medium was increased by selective solvents such as O-dichlorobenzene, p-chlorotoluene and nitrobenzene,

the rate was found to increase with increase in the dielectric constant of the solvent, but the molecular weight of the polymer was unaffected. Morton and Bostick[27] found that tetrahydrofuran (THF) also had a very marked effect of increasing the rate of polymerization of octomethylcyclotetrasiloxane catalyzed by KOH. However they noted that since the dielectric constant of THF is much lower than other solvents like nitrobenzene, the very marked increase in rate caused by THF must be ascribed to some other effect, such as the ion solvation phenomenon. They also found that the observed rate constant showed a linear dependency upon the square root of catalyst concentration showing that the silanolate anion was in equilibrium with the undissociated potassium silanolate.

Cooper and Elliott[28] studied the effects of small amounts (0.01-1%) of dimethylsulfoxide (DMSO) on base-catalyzed polymerization of octamethylcyclotetrasiloxane. They determined the time required to produce a stiff gum at a particular catalyst (KOH) concentration as a function of DMSO concentration. Increasing the DMSO concentration reduced dramatically the time taken to form a stiff gum. They also found that the rate enhancement for a particular amount of DMSO (0.5%) was higher at lower catalyst concentration. They explained the accelerating effect of DMSO as due to solvation of the cation which promoted the ionization of the metal silanolate, increasing the concentration of silanolate anions. Ostrozynski[25] studied the effects of hexamethylphosphoramide (HMPA), tributylphosphine oxide and triethylphosphate on the potassium silanolate catalyzed polymerization of octamethylcyclotetrasiloxane. He found that HMPA was the most active promoter

of the three. With as little as 0.5% promoter, polymerization proceeded nearly two times faster at 50° than did the unpromoted polymerization at 140°. He ascribed the acceleration in rate by the addition of small amounts of promoter to the formation of a more reactive initiating entity viz., solvent separated ion pairs which coexist in equilibrium with relatively inactive intimate ion pairs. Yuzhelevskii et al.[29] studied the anionic polymerization of methyl(propyl)cyclosiloxanes both in bulk as well as in acetone solutions utilizing potassium silanolate as the catalyst. They reported that in the bulk polymerization the rate constant was directly proportional to the square root of the catalyst concentration, while in acetone solution the rate constant was directly proportional to the catalyst concentration. Yuzhelevskii et al.[30] studied the effectiveness of various promoters in the anionic polymerization of 2,4,6-tris(3,3,3-trifluoropropyl)-2,4,6-trimethylcyclotrisiloxane $[CH_3Si(CH_2CH_2CF_3)O]_3$. They found that the rate of polymerization increased with increasing promoter concentration at a constant catalyst concentration, whereas when catalyst concentration was varied at a constant promoter concentration, the rate of polymerization reached a maximum after which the rate decreased as the catalyst concentration was increased further.

3. Acid-Catalyzed Polymerizations

Mineral acids[31,32,33] and Lewis acids[33] have been utilized as catalysts for the conversion of low molecular weight organocyclosiloxanes to high polymers. Scott[31] utilized concentrated sulfuric acid, anhydrous hydrogen chloride and antimony pentachloride to polymerize octamethylcyclotetrasiloxane. Andrianov et al.[34] utilized

stannic chloride for the polymerization of octamethylcyclotetrasiloxane. Most of the mechanistic studies on the acid-catalyzed polymerization were conducted on sulfuric acid-catalyzed polymerization of octamethylcyclotetrasiloxane. Patnode and Wilcock[32] postulated the following reaction path for the sulfuric acid/octamethylcyclotetrasiloxane system.

$$[(Me)_2SiO]_4 + HO\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}OH \longrightarrow$$

$$HO(Me)_2Si\text{-}O\text{-}(Me)_2Si\text{-}O\text{-}(Me)_2Si\text{-}O\text{-}Si(Me)_2OSO_2H$$

(I)

$$(\sim Si(Me)_2OH)_2 \xrightarrow[H(+)]{} \sim Si(Me)_2\text{-}O\text{-}Si(Me)_2\sim + H_2O$$

$$\sim Si(Me)_2OSO_2H + H_2O \longrightarrow \sim Si(Me)_2OH + H_2SO_4$$

The chain growth and consequent increase in molecular weight from the intermediate species (I) were visualized as occurring by terminal silanol condensation to eliminate water which hydrolyzed the sulfate ester end group to regenerate silanol for further condensation. Hurd[33] investigated the above polymerization reaction and proposed the concept of multistep addition polymerization with the formation of protonated siloxonium ion as the active chain end. Initial ring-opening results in the formation of protonated siloxonium ion as follows:

$$[(Me)_2SiO]_4 + H^+ \longrightarrow -(Me)_2Si\text{-}\overset{(+)}{\underset{\underset{H}{|}}{\ddot{O}}}\text{-}Si(Me)_2-$$

in which the silicon atoms are susceptible to nucleophilic attack by non-protonated siloxane molecules. The literature survey reveals that the mechanism of acid-catalyzed polymerization is not clearly understood.

D. POLYMERIZATION OF CYCLOCARBOSILOXANES

The homopolymerization studies of 5-membered cyclocarbosiloxanes reported in the literature have all been qualitative. Piccoli et al.[7] reported that the 5-membered cyclocarbosiloxanes can be polymerized to high polymers using a trace of potassium dimethylsilanolate catalyst. In the series of C-substituted 5-membered cyclocarbosiloxanes, Polyakova et al.[18] found that the monosubstituted compounds of the type $(CH_3)(R)\overline{SiCH(x)CH(X)SiO}(R)(CH_3)$, (where x = C_4H_9, α-$C_{10}H_{17}$ or C_6H_5) polymerized in the presence of H_2SO_4 or KOH, yielding oily products. In contrast to the monosubstituted derivatives, they found that the cyclocarbosiloxanes disubstituted at carbon atoms did not polymerize under the influence of acids or bases. Andrianov et al.[35] found that the rate of polymerization of the 6-membered cyclocarbosiloxane $(CH_3)_2\overline{SiCH_2CH_2CH_2SiO}(CH_3)_2$ in the presence of KOH and H_2SO_4 was 100 times lower than the rate of polymerization of hexamethylcyclotrisiloxane. They determined an activation energy of 21 kcal/mole for the anionic polymerization and 7 kcal/mole for the cationic polymerization. They found that the intrinsic viscosity of the polymers increased linearly with percent conversion, and in the initial stages the reaction was first order with respect to the monomer.

Andrianov et al.[36] studied the effect of the substituent at the silicon atom on the rate of polymerization of the 6-membered cyclocarbosiloxanes. They found in the presence of KOH, when the methyl groups

were replaced by higher alkyl groups, the rate of polymerization was lowered by a factor of 10 while the introduction of the phenyl group increased the rate of reaction somewhat. In the case of cationic polymerization, they found that not only the aryl substituents but also the higher alkyl substituents lowered the rate. This was explained as due to swamping of the inductive effect by the steric effect.

In the case of higher membered cyclocarbosiloxanes of the above type, no study on their hompolymerization has appeared in the literature. Homopolymerization of other types of cyclocarbosiloxanes have all been qualitative and can be found in the review[8].

E. PREPARATION OF MONODISPERSED POLYDIMETHYLSILOXANES

Lee and his co-workers[37] found that strained cyclosiloxanes like hexamethylcyclotrisiloxane can be converted to essentially monodispersed polymers by using lithium bases as catalysts, in the presence of DMSO as a promoter. These bases like lithium hydroxide, lithium silanolate, and butyllithium do not participate in the rearrangement of linear siloxanes. Lee and his co-workers made the following observations:

(i) The rate of polymerization of hexamethylcyclotrisiloxane was first order with respect to monomer.

(ii) The rate increased with increasing amounts of DMSO.

(iii) The amount of water in the system did not affect the rate significantly, but the molecular weight and molecular weight distribution depended upon the amount of water.

The literature survey reveals that strained cyclosiloxanes can be polymerized to essentially monodispersed polymers[37]. The 5-membered

cyclocarbosiloxanes 2,2,5,5 tetraorgano-1-oxa-2,5-disilacyclopentane, $(R)_2\overline{SiCH_2CH_2Si(R)_2O}$, are known to be strained and are known to polymerize. However, there has not been a detailed study performed on the homopolymerization of these cyclocarbosiloxanes. The results reported in this dissertation encampass an investigation of the base-catalyzed ring-opening polymerization of a series of 5-membered cyclocarbosiloxanes.

III. EXPERIMENTAL

A. GENERAL

The melting points of solid materials were determined using a Mettler FP-1 melting and boiling point apparatus, and are reported here uncorrected. The boiling points reported were those at which the fraction was collected (5-95%). The structures of the silanes used were confirmed by NMR spectra using a Varian EM 360 NMR Spectrometer. Both chloroform and tetramethylsilane were used as reference standards. Chemical shifts reported in this work are in parts per million with reference to the tetramethylsilane peak at $\delta = 0.0$. Infrared spectra of the monomers were recorded on a Beckman IR-12 Infrared Spectrophotomer. The assignment of infrared bands both in the cyclic monomers and in the linear polymers was based on Colthup's correlation charts[38] and charts by Noll[39]. Gas-liquid chromatography (GLC) analyses of the monomers were performed using an Aerograph HY-F1 model 600-D instrument fitted with a 5 feet x 1/8 inch column packed with SE-30 on Chromosorb W and employing a flame ionization detector. The purity of the monomers was greater than 99%. The densities and refractive indices of the monomers were determined at 20^{o}. The physical properties of the monomers are tabulated in Table I.

Methyldichlorosilane, dimethylchlorosilane, vinyldimethylethoxysilane and methylvinyldichlorosilane were obtained commercially and used as received. All other chlorosilanes were prepared by Grignard synthesis.

TABLE I

PHYSICAL CONSTANTS OF MONOMERS

Monomer	Structure	BP	Density $\frac{20}{4}$ g/cm^3	Refractive index	Molar Refraction* observed	calculated
Cyclic A	$(Me)_2\overline{SiCH_2CH_2Si(Me)_2O}$	124°/734 torr	0.8620	1.4179	46.85	46.77
Cyclic B	$(Ph)(Me)\overline{SiCH_2CH_2Si(Me)_2O}$	131°/30 torr	0.9776	1.4979	66.64	67.12
Cyclic C	$(Ph)(Me)\overline{SiCH_2CH_2Si(Ph)(Me)O}$	132°/0.5 torr	1.0518	1.5512	86.27	86.95
Cyclic D	$(Ph)_2\overline{SiCH_2CH_2Si(Me)_2O}$	178-180°/10 torr	1.0510	1.5510	86.30	86.95
Cyclic E	$(Ph)(Me)\overline{SiCH_2CH_2Si(Ph)_2O}$	188-190°/1 torr	1.0955	1.5890	106.53	106.78
Cyclic F	$(Ph)_2\overline{SiCH_2CH_2Si(Ph)_2O}$	77.7° (mp)	--	--	--	--

*Methods for obtaining molar refractions (observed and calculated) are shown in Appendix A.

B. PREPARATION OF CHLOROSILANES

1. The Preparation of Phenylmethylvinylchlorosilane

A 118 g (0.84 mole) sample of methylvinyldichlorosilane was dissolved in 1 liter of tetrahydrofuran (THF) at 60°. A solution of 0.84 moles of phenylmagnesium chloride in THF (Fisher Chemicals) was added dropwise with vigorous stirring. After the addition of phenylmagnesium chloride, the mixture was further refluxed for 6 hours. After cooling the mixture and allowing the salt to settle, the supernatant liquid was decanted and the salt washed with THF. The solvent was stripped by distillation at atmospheric pressure and the remaining liquid fractionated in a Nester-Faust auto annular still. A total of 103 g (67%) of phenylmethylvinylchlorosilane was collected at 105°/25 torr, d_4^{20} = 1.0368 (lit.[40] d_4^{25} = 1.0340, bp 79-79.5°/3-4 torr). Infrared spectrum (neat) showed among other bands, bands at 3000-3100 cm^{-1} (C-H, aromatic), 2900-3000 cm^{-1} (C-H, aliphatic), 1595 cm^{-1} (C=C), 1430 cm^{-1} (C_6H_5) 1120 cm^{-1} (Si-C_6H_5), 1258 cm^{-1} (Si-CH_3) and 540 cm^{-1} (Si-Cl).

2. The Preparation of Phenylmethylchlorosilane

A mixture of dry diethyl ether and 48 g (2 moles) of magnesium turnings was placed in a 3 liter, 3-necked round bottomed flask fitted with a water condenser, drying tube, mechanical stirrer and a 500 ml pressure equalizing dropping funnel. The mixture was stirred as a solution of 314 g (2 moles) of bromobenzene in 1 liter of dry diethyl ether was added by means of the dropping funnel. The rate of addition of bromobenzene solution was controlled so as to maintain a gentle ether reflux. After the addition of the bromobenzene solution,

the brown solution was stirred for an hour more and the phenylmagnesium bromide solution was decanted from the unreacted magnesium turnings (5 g).

A solution of 205 g (1.8 moles) of methyldichlorosilane in 200 ml dry diethyl ether was taken in a 3 liter, 3-necked indented flat bottomed flask fitted with a mechanical stirrer, water condenser, drying tube, and a 500 ml pressure equalizing dropping funnel. The flask was set inside an ice bath. The phenylmagnesium bromide solution prepared above was added dropwise with vigorous stirring. After the addition of phenylmagnesium bromide solution, the mixture was stirred for 2 hours more and the salt allowed to settle. The supernatant liquid was decanted and the salt washed with diethyl ether. The washings were combined with the mother liquor and the diethyl ether distilled from the solution. The remaining liquid was fractionated under vacuum in a Nester-Faust auto annular still. Phenylmethylchlorosilane (105 g; 38%) distilling at $102^{o}/70$ torr (lit.[41] bp $113^{o}/100$ torr) was collected. The NMR spectrum (CCl_4) showed a multiplet centered at 7.4 δ (5H, Si-C_6H_5) a quartet at 5.26 δ (1H, Si-H) and a doublet at 0.68 δ (3H, Si-CH_3).

3. The Preparation of Phenylvinyldichlorosilane

Magnesium turnings (100 g, 4.17 moles) were placed in a dry 3 liter, 3-necked round bottomed flask fitted with a condenser, drying tube, mechanical stirrer and a dropping funnel. A solution of 50 g of chlorobenzene (0.4 mole) and 50 g of dry THF was added, along with a crystal of iodine to initiate the formation of phenylmagnesium chloride. The contents were warmed until the brown color of phenylmagnesium chloride appeared. A total of 398 g (3.6 moles) chlorobenzene

in 2.6 liter THF was added dropwise maintaining a gentle reflux of THF. After the addition of all the chlorobenzene, the mixture was cooled and decanted into a well dried amber colored bottle. The concentration of phenylmagnesium chloride in THF was approximately 4 moles/liter.

A solution of 320 g (2.0 moles) of vinyltrichlorosilane and 1 liter of heptane was taken in a dry 3 liter, 3-necked flask fitted with a water condenser, drying tube, mechanical stirrer and a dropping funnel. To this mixture, 2.0 moles of phenylmagnesium chloride solution was added at room temperature with vigorous stirring. After the addition, the mixture was stirred at THF reflux for 2 hours more, cooled and the salt allowed to settle. The supernatant liquid was decanted, the salt washed with THF and the solvent from the combined washings was distilled at atmospheric pressure. The residue after solvent distillation was fractionated under vacuum in a Nester-Faust auto annular still. Phenylvinyldichlorosilane (211 g, 52%) was collected at 102-104°/13 torr, (lit.[42] bp 84-87°/1.5 torr) and diphenylvinylchlorosilane (26.5 g, 10.0%) at 122-125°/0.5 torr (lit.[42] bp 133-136°/1.5 torr). The NMR spectrum (CCl_4) of phenylvinyldichlorosilane showed a multiplet centered at 7.5 δ (5H, SiC_6H_5) and a multiplet centered at 6.1 δ (3H, $Si\text{-}CH{=}CH_2$).

4. The Preparation of Diphenylvinylchlorosilane

To a mixture of 202 g (1 mole) of phenylvinyldichlorosilane and 1 liter of dry THF at 60°, 1 mole of phenylmagnesium chloride solution was added as described before. After the addition, the mixture was stirred at THF reflux for 8 hours more, cooled and worked up as described in the preparation of phenylvinyldichlorosilane. The residue remaining after removing THF was fractionated in a Nester-Faust auto

annular still under vacuum. Diphenylvinylchlorosilane (116 g 44%) distilling at 122-125°/0.5 torr was collected. The NMR spectrum (CCl_4) showed multiplets centered at 7.50 δ (10H, Si-C_6H_5) and at 6.20 δ (3H, Si-CH=CH_2).

5. The Preparation of Diphenylchlorosilane

A dry liter, 3-necked flask was fitted with a condenser, drying tube, mechanical stirrer and a dropping funnel. A solution of 250 ml anhydrous diethyl ether and 250 ml dry benzene was placed in the flask and cooled to 0° by means of an ice bath. A total of 200 g (1.5 moles) of trichlorosilane was added and the solution stirred as 3.0 moles of phenylmagnesium bromide in ether (prepared as described in the preparation of phenylmethylchlorosilane) were added dropwise. After the addition, the mixture was stirred for 2 hours more and worked up as described in the preparation of phenylmethylchlorosilane. After removing diethyl ether and benzene, the residual liquid was fractionated in a Nester-Faust auto annular still under vacuum. A total of 106 g (32%) of diphenylchlorosilane was collected at 125°/4 torr (lit.[41] bp 143°/10 torr). NMR spectrum (CCl_4) showed a multiplet centered at 8.35 δ (10H, Si-C_6H_5) and a singlet at 6.2 δ (SiH).

C. HYDROSILATION ADDITION REACTIONS

1. The Preparation of Hydrosilation Catalyst

The catalyst for the hydrosilation addition reaction was prepared by dissolving 1.0 g of chloroplatinic acid in 19.3 g isopropyl alcohol to give a 0.1M solution. A 10 µl sample of the catalyst solution was equivalent to 10^{-6} mole Pt. All additions of the catalyst were made from the same 50 µl syringe.

2. The Preparation of the Mixture of 1,2-Bis(dimethylchlorosilyl) ethane, 1,2-Bis(dimethylethoxysilyl)ethane and 1-(Dimethylchlorosilyl)-2-(dimethylethoxysilyl)ethane

A mixture of 156 g (1.2 moles) of vinyldimethylethoxysilane and 50 μl chloroplatinic acid was placed in a 500 ml 3-necked flask fitted with a water condenser, magnetic stirrer, dropping funnel and a thermometer. The mixture was heated to 75° by means of a heating mantle and 114 g (1.2 moles) of dimethylchlorosilane was added dropwise. The temperature of the exothermic reaction was maintained at 120° by controlling the addition rate. After the addition of chlorosilane was completed, the mixture was stirred for 5 minutes more and the crude adduct distilled through a 6 inch Vigreux column. The adduct collected between 190-195° at atmospheric pressure amounted to 240 g. The NMR spectrum (CCl_4) of the adduct had singlets at 0.00, 0.40, 0.43 and 0.83 δ and a multiplet centered at 0.54 δ. From the complex NMR spectrum it was concluded that the adduct was a mixture of compounds. In order to separate and identify the components, the hydrosilation addition reaction was repeated using 0.2 mole of reactants under a nitrogen atmosphere. After the addition reaction was completed, the mixture was fractionated in a Nester-Faust auto annular still with a reflux ratio of 200:1 and the teflon band spinning at 7200 rpm. 1,2-Bis(dimethylchlorosilyl)ethane was collected as a solid adduct at 190°/50 torr. Recrystallization from n-pentane yielded the pure compound melting at 36° (lit.[7] mp 37°). The NMR spectrum (CCl_4) had singlets at 0.4 δ (12H, Si-CH_3) and 0.83 δ (4H, -CH_2CH_2-). The second fraction collected at 113°/50 torr was found by NMR analysis to be a mixture of 1,2-bis(dimethylchlorosilyl)ethane (I), 1,2-bis(dimethylethoxysilyl)ethane (II) and 1-(dimethylchlorosilyl)-2-(dimethyl-

ethoxysilyl)ethane (III). Repeated fractionation gave the unsymmetrical adduct (III) in 70% purity. The NMR spectrum (CCl_4) of this fraction had a $-CH_2CH_2-$ multiplet centered at 0.54 δ. The third fraction, 1,2-bis(dimethylethoxysilyl)ethane, was collected at 116°/50 torr (n_D^{20} 1.4205), Anal. calcd for $C_{10}H_{26}O_2Si_2$: C, 51.19: H, 11.18; Si, 23.97. Found: C, 51.00; H, 11.08; Si, 23.97. The NMR spectrum (CCl_4) had singlets at 0.00 δ (12H, $Si-CH_3$) and 0.43 δ (4H, $-CH_2CH_2-$), a triplet at 1.1 δ (3H, $Si-OC_2H_5$) and a quartet at 3.6 δ (2H, $Si-OC_2H_5$). Thus it was concluded that the adduct collected between 190-195° at atmospheric pressure was a mixture of I, II and III.

3. The Preparation of 1-Dimethylchlorosilyl-2-phenylmethylchlorosilylethane

A mixture of 168 g (0.93 mole) phenylmethylvinylchlorosilane and 30 μl chloroplatinic acid solution was placed in a 500 ml 3-necked flask fitted with a thermometer, magnetic stirrer and a 500 ml pressure equalizing funnel. The mixture was initially heated to 75°, and 99 g (1.05 moles) of dimethylchlorosilane was added dropwise. The temperature of the reaction was maintained at 120° by maintaining the rate of addition of dimethylchlorosilane. After the addition of dimethylchlorosilane, distillation of the liquid adduct through a Nester-Faust auto annular still yielded 239 g (93%) at 150°/10 torr (lit.[7] bp 191°/50 torr) of the adduct 1-dimethylchlorosilyl-2-phenylmethylchlorosilylethane. The NMR spectrum (CCl_4) showed a multiplet centered at 7.40 δ (5H, SiC_6H_5), a multiplet centered at 0.90 δ (4H, $-CH_2-CH_2-$) and singlets at 0.65 δ (3H, $Si-CH_3$), 0.40 δ (6H, $CH_3-Si-CH_3$).

4. The Preparation of 1,2-Bis(phenylmethylchlorosilyl)ethane

To a mixture of 200 g (1.1 moles) phenylmethylvinylchlorosilane and 100 μl chloroplatinic acid at 125°, 172 g (1.1 moles) of

phenylmethylchlorosilane was added dropwise as described in the preparation of 1-dimethylchlorosilyl-2-phenylmethylchlorosilylethane. The temperature was maintained at 135° by controlling the rate of addition of phenylmethylchlorosilane. The crude adduct was distilled under vacuum through a 4 inch distillation column. The adduct 1,2-bis-(phenylmethylchlorosilyl)ethane which crystallized in the receiver was collected at 162-165°/1 torr. The solid was recrystallized from pentane to obtain 279 g (75%) of the adduct with mp 67.2° (lit.[7] mp 68°).

5. The Preparation of 1-Dimethylchlorosilyl-2-diphenylchlorosilylethane

To a mixture of 100 g (0.41 mole) of diphenylvinylchlorosilane and 30 μl chloroplatinic acid solution at 110°, 39 g (0.41 mole) of dimethylchlorosilane was added dropwise as described in the preparation of 1-dimethylchlorosilyl-2-phenylmethylchlorosilylethane. The temperature was maintained at 135° by controlling the rate of addition of dimethylchlorosilane. After the addition, the mixture was heated to 145° and maintained at that temperature for 2 hours to ensure completion of the reaction. The crude adduct was fractionated under vacuum through a 4 inch column to yield 108 g (78%) of 1-dimethylchlorosilyl-2-diphenylchlorosilylethane at 175°/1.0 torr (lit.[7] bp 2.5/10 torr). The NMR spectrum (CCl_4) showed a multiplet centered at 7.40 δ (10H, Si-C_6H_5), a multiplet centered at 1.15 δ (4H, -CH_2-CH_2-) and a singlet at 0.40 δ (6H, Si-CH_3).

6. The Preparation of 1-Phenylmethylchlorosilyl-2-diphenylchlorosilylethane

To a mixture of 61 g (0.33 mole) phenylmethylvinlychlorosilane and 20 μl chloroplatinic acid solution at 110°, 73 g (0.33 mole) of

diphenylchlorosilane was added dropwise as described in the preparation of 1-dimethylchlorosilyl-2-phenylmethylchlorosilylethane. After the addition of diphenylchlorosilane, the solution was stirred for 2 hours more at 145° and the crude adduct distilled under vacuum through a 4 inch column. The adduct 1-phenylmethylchlorosilyl-2-diphenylchlorosilylethane (100 g, 71%) was collected at 210-215°/1 torr (lit.[7] bp 256°/8 torr). NMR spectrum (CCl_4) showed multiplets centered at 7.50 δ (15H, Si-C_6H_5) and 1.30 δ (4H, -CH_2CH_2-) and a singlet at 0.60 δ (3H, Si-CH_3).

7. The Preparation of 1,2-Bis(diphenylchlorosilyl)ethane

To a mixture of 73 g (0.3 mole) diphenylvinylchlorosilane and 50 μl chloroplantinic acid solution at 115°, 66 g (0.3 mole) diphenylchlorosilane were added dropwise as described in the preparation of 1-dimethylchlorosilyl-2-phenylmethylchlorosilylethane. After the addition of diphenylchlorosilane, the mixture was stirred at 120° for 3 hours and at 150° for another 90 minutes to ensure completion of the addition reaction. The crude adduct was distilled under vacuum through a 4 inch column. The adduct 1,2-bis(diphenylchlorosilyl)ethane was collected at 230-234°/0.4 torr which crystallized in the receiver. Recrystallization from hexane yielded 102 g (73%) of the solid adduct with a mp 95° (lit.[7] mp 98°).

D. CYCLIZATION REACTIONS

1. The Preparation of 2,2,5,5-Tetramethyl-1-oxa-2,5-disilacyclopentane (Cyclic A)

Distilled water (200 ml) was measured into a 1 liter 3-necked jacketed flask fitted with a thermometer, magnetic stirrer and dropping

funnel and 162 g of the mixture of adducts 1,2-bis-(dimethylchlorosilyl) ethane, 1,2-bis-(dimethylethoxysilyl)ethane and 1-(dimethylchlorosilyl)-2-(dimethylethoxysilyl)ethane was added dropwise with stirring. The temperature of the reaction was maintained between 15-20° by circulating tap water through the water jacket. After hydrolysis, 250 ml of 2:1 benzene-ether solution was added to dissolve the viscous hydrolysate. The mixture was transferred to a 2 liter separatory funnel, the aqueous layer drawn off and the organic layer washed with distilled water until the washings were neutral to pH paper. The hydrolysate solution was stored over molecular sieves to remove residual water, and then taken in a tarred 500 ml round bottomed flask fitted with a thermometer well. Ether and benzene were stripped from the hydrolysate by distillation at atmospheric pressure. The yield of hydrolysate was 125 g.

The 500 ml round bottomed flask containing the hydrolysate was fitted with a distillation head, condenser and receiver, and a thermometer was placed in the thermometer well. To 125 g of the hydrolysate 0.9 g of powdered KOH was added and pyrolysed at 220-280° by heating the flask by means of a heating mantle. The yield of crude cyclic was 112 g, which was fractionated twice through a 12 inch Vigreux column at atmospheric pressure. Cyclic A (72 g, 58.7%) distilling at 122-124°/734 torr (lit.[7] 124°/735 torr) was collected. The infrared spectrum (neat) among other bands showed bands at 924 cm^{-1} (s, Si-O-Si) 1255 cm^{-1} (s, $Si-CH_3$), 795 cm^{-1} (s,$CH_3-Si-CH_3$) and 1070 cm^{-1} (m, $-SiCH_2-$). The NMR spectrum (CCl_4) showed singlets at 0.68 δ (4H, $-CH_2-CH_2-$) and 0.05 δ (12H, $Si-CH_3$).

2. The Preparation of 2,2,5-Trimethyl-5-phenyl-1-oxa-2,5-disilacyclopentane (Cyclic B)

To a hetergeneous solution of 130 ml toluene and 200 ml distilled water, 223 g (0.8 mole) of 1-dimethylchlorosilyl-2-phenylmethylchlorosilylethane was added dropwise with stirring. The hydrolysate solution was worked up as described for the cyclic A preparation yielding 185 g of the hydrolysate as an elastic gum which was pyrolysed at 310° in the presence of 1.0 g lithium hydroxide. The crude cyclic B collected amounted to 160 g which was fractionated under vacuum through a 6 inch Vigreux column yielding 130 g (70%) of cyclic B at 131°/30 torr (lit.[7] bp 146°/50 torr). The infrared spectrum (neat) showed among other bands, bands in the region 3000-3100 cm^{-1} (m, C-H aromatic) 2880-3000 cm^{-1} (m, C-H aliphatic), 1590 cm^{-1} (w, -C = C-), 1430 cm^{-1} (s, C_6H_5), 1252 cm^{-1} (s, Si-CH_3), 1118 cm^{-1} (s, Si-C_6H_5), 920 cm^{-1} (s, Si-O-Si) and 860 cm^{-1} (s, CH_3-Si-CH_3). The NMR spectrum (CCl_4) showed multiplets centered at 7.30 δ (5H, Si-C_6H_5), and 0.85 δ (4H, -CH_2-CH_2) and singlets at 0.35 δ (3H, Si-CH_3) and 0.20 δ (6H, CH_3-Si-CH_3).

3. The Preparation of 2,5-Dimethyl-2,5-diphenyl-1-oxa-2,5-disilacyclopentane (Cyclic C)

1,2-Bis(phenylmethylchlorosilyl)ethane (265 g, 0.78 mole) was dissolved in toluene and hydrolyzed with about 500 ml distilled water, and the hydrolysate worked up as described for cyclic A. The acid-free hydrolysate (230 g) was pyrolyzed in the presence of 0.6 g of lithium hydroxide at 275-300° under a vacuum of 1 torr. The crude cyclic C was fractionated under vacuum through a 6 inch Vigreux column. At 132°/0.5 torr (lit.[7] bp 182°/10 torr) 145 g (63%) of the cyclic was collected. The infrared spectrum (neat) showed among other bands, bands in the region 3000-3100 cm^{-1} (m, C-H aromatic), 2880 to 3000 cm^{-1}

(m, C-H aliphatic) 1590 cm^{-1} (m, -C=C-), 1255 cm^{-1} (s, Si-CH_3), 1430 cm^{-1} (s, C_6H_5), 1120 cm^{-1} (s, Si-C_6H_5) and 915 cm^{-1} (s, SiOSi). The NMR spectrum (CCl_4) showed a multiplet centered at 7.40 δ (10H, Si-C_6H_5), a doublet at 1.10 δ (4H, -CH_2-CH_2-) and a doublet at 0.43 δ (6H, Si-CH_3). The doublets in -CH_2-CH_2- and Si-CH_3 peaks arise because of the cis-trans configuration of the monomer, the cis peaks being shifted upfield. The cyclic 'C' was analyzed by GLC with the column operating at 215°. The GLC analysis indicated that the cyclic 'C' was approximately 55:45 mixture of cis and trans isomers.

4. The Preparation of 2,2-Dimethyl-5,5-diphenyl-1-oxa-2,5-disilacyclopentane (Cyclic D)

1-Dimethylchlorosilyl-2-diphenylchlorosilylethane (100 g, 0.29 mole) was hydrolyzed in a heterogeneous solution of 300 ml water and 200 ml toluene, and the hydrolysate worked up as described for cyclic A. After distilling the solvent, 90 g of the hydrolysate was pyrolyzed in the presence of 0.9 g of lithium hydroxide at 300°, under a vacuum of 1 torr. The crude cyclic D collected upon pyrolysis was fractionated under vacuum through a 6 inch Vigreux column. Cyclic D (47 g; 52%) was collected at 136°/1 torr (lit.[7] bp 181°/11 torr). Infrared spectrum (neat) showed among other bands, bands at 3000-3100 cm^{-1} (m, C-H, aromatic), 2800-3000cm^{-1} (m, C-H aliphatic), 1590 cm^{-1} (m, -C=C-), 1430 cm^{-1} (s, C_6H_5) 1120 cm^{-1} (s, Si-C_6H_5), 1250 cm^{-1} (s, Si-CH_3), 920 cm^{-1} (s, Si-O-Si) and 850 cm^{-1} (s, CH_3-Si-CH_3). The NMR spectrum (CCl_4) showed multiplets centered at 7.65 δ (10H, Si-C_6H_5) and 1.33 δ (4H, -CH_2CH_2-) and a singlet at 0.52 δ (6H, CH_3-Si-CH_3).

5. The Preparation of 2-Methyl-2,5,5-triphenyl-1-oxa-2,5-disilacyclopentane (Cyclic E)

The adduct 1-phenylmethylchlorosilyl-2-diphenylchlorosilylethane (96 g 0.25 mole) was dissolved in 100 ml toluene and hydrolyzed in 200 ml of 1:1 toluene-water mixture. The hydrolysate solution was worked up as described for cyclic A and 87 g of the acid-free hydrolysate was pyrolysed under a vacuum of 1 torr at 300° in the presence of 0.3 g lithium hydroxide. The crude cyclic E was fractionated under vacuum through a 6 inch Vigreux column. Cyclic E (55 g, 71%) was collected at 170°/0.3 torr (lit.[7] bp 241°/11 torr). Infrared spectrum (neat) showed among other bands, bands at 3000-3100 cm^{-1} (m, C-H, aromatic), 3880-2980 cm^{-1} (m, C-H, aliphatic), 1590 cm^{-1} (m, C=C), 1430 cm^{-1} (s, C_6H_5), 1120 cm^{-1} (s, Si-C_6H_5) 1257 cm^{-1} (s, Si-CH_3) and 915 cm^{-1} (s, Si-O-Si). The NMR spectra (CCl_4) showed multiplets centered at 7.50 δ (15H, Si-C_6H_5), and 1.20δ (4H, -CH_2-CH_2-) and a singlet at 0.49 δ (3H, Si-CH_3).

6. The Preparation of 2,2,5,5-Tetraphenyl-1-oxa-2,5-disilacyclopentane (Cyclic F)

The solid adduct 1,2-bis-(diphenylchlorosilyl)ethane (97 g 0.21 mole) was dissolved in hot toluene and hydrolyzed in 200 ml water. The hydrolysate was worked up as described for Cyclic A and the acid free hydrolysate (89 g) was pyrolyzed at about 350° under a vacuum of 1 torr in the presence of 0.25 g lithium hydroxide. The crude cyclic F was obtained as a solid which was recrystallized twice from hexane. Cyclic F (40 g, 44%) was obtained as white needles with a mp 77.7° (lit.[7] mp 80°). Infrared spectrum (KBr pellet, 10% conc.) showed among other bands, bands at 3000-3100 cm^{-1} (m, C-H, aromatic), 2860-2960 cm^{-1} (w, C-H, aliphatic), 1590 cm^{-1} (m, C=C), 1430 cm^{-1} (s, C_6H_5)

1120 cm^{-1} (s, Si-C_6H_5) and 910 cm^{-1} (s, Si-O-Si). The NMR spectrum (CCl_4) showed a multiplet centered at 7.40 δ (20H, Si-C_6H_5) and a singlet at 1.37 δ (4H, -CH_2-CH_2-). The molecular weight of the cyclic F was 400 (calcd. 410) as determined by vapor phase osmometry.

7. Handling and Storage of Monomers

These cyclic monomers were found to be very sensitive to trace amounts of acids and bases and would polymerize upon standing if contaminated. Efforts to store cyclic A over molecular sieves resulted in the formation of a viscous material after a period of 1 month. A sample of cyclic D polymerized in the bottle in which it was stored. These samples were discarded.

It was found therefore imperative to store these cyclic monomers in containers which were washed thoroughly with distilled water without any acid or base treatment of the container.

E. BASE CATALYZED POLYMERIZATIONS

Preliminary experiments were conducted on the base-catalyzed polymerization of cyclic monomers using a variety of lithium bases such as n-butyllithium, lithium silanolates and THF as a promoter. These experiments were conducted both in a 50 ml 3-necked flask fitted with a water jacket and in an NMR tube. These experiments were aimed mainly to obtain the polymers that can be characterized by IR and NMR spectrometry.

1. Polymerization of Cyclic A

In a dry 50 ml 3-necked flask fitted with a water jacket, 8.0 g (0.05 mole) of cyclic A was taken as a 50 wt % solution in THF. The solution was thermostated at 25^{o} by circulating an ethylene glycol

water mixture from a constant temperature bath. A gentle flow of dry argon was maintained over the solution. By means of a microsyringe 5 μl (11.23×10^{-6} mole) of n-butyllithium solution was added. A visible increase in the viscosity of the solution was seen after 5 minutes. After stirring for 60 minutes, the polymerization reaction was quenched with a drop of glacial acetic acid and the polymer precipitated in methanol, redissolved in benzene and freeze-dried. The infrared spectrum (neat) was obtained by spreading a thin film of the polymer dissolved in CCl_4 over a KBr plate and allowing the solvent to evaporate. The spectrum showed bands at 2880-2980 cm^{-1} (C-H, aliphatic), 1255 cm^{-1} (s, $Si-CH_3$) and 1050-1080 cm^{-1} (s, Si-O-Si). The NMR spectrum (CCl_4) showed singlets at 0.40 δ ($-CH_2-CH_2$) and 0.00 δ ($Si-CH_3$).

2. Polymerization of Cyclic B

The polymerization of cyclic B was conducted exactly as described for cyclic A. The infrared spectrum showed bands at 3000-3100 cm^{-1} (C-H, aromatic), 2880-2980 cm^{-1} (C-H, aliphatic), 1595 cm^{-1} (C=C), 1120 cm^{-1} ($Si-C_6H_5$), 1258 cm^{-1} ($SiCH_3$) and 1050-1090 cm^{-1} (Si-O-Si) among other bands. The NMR spectrum (CCl_4) had a multiplet centered at 7.32 δ ($Si-C_6H_5$) and 0.60 δ ($-CH_2CH_2$), a singlet at 0.35 δ ($Si-CH_3$) and a doublet at 0.10 δ ($CH_3-Si-CH_3$).

3. Polymerization of Cyclic C

The polymerization of cyclic C was conducted exactly as described for cyclic A. The infrared spectrum showed bands at 3000-3100 cm^{-1} (C-H, aromatic), 2860-2980 cm^{-1} (C-H, aliphatic) 1580 cm^{-1} (-C=C-), 1120 cm^{-1} ($Si-C_6H_5$), 1255 cm^{-1} ($Si-CH_3$) and 1030-1100 cm^{-1} (Si-O-Si) among other bands. The NMR spectrum (CCl_4) had a multiplet

centered at 7.30 δ ($Si-C_6H_5$) and singlets at 0.62 δ ($-CH_2-CH_2-$) and 0.22 δ ($Si-CH_3$).

4. Polymerization of Cyclic D

The polymerization of cyclic D was conducted in an NMR tube. A solution of 345 μl (0.125×10^{-2} mole) of cyclic D in 900 μl of benzene and 300 μl of THF was taken in an NMR tube. To this solution 3.5×10^{-6} mole of lithium n-butyldiphenylsilanolate solution was added and cyclic D was polymerized for 24 hours at 31.7°. The polymerization was quenched with a drop of glacial acetic acid and the polymer was precipitated in methanol and dried. The infrared spectrum (neat) showed bands at 2980-3080 cm^{-1} (C-H, aromatic), 2860-2960 cm^{-1} (C-H, aliphatic), 1580 cm^{-1} (-C=C-), 1120 cm^{-1} ($Si-C_6H_5$), 1255 cm^{-1} ($Si-CH_3$) and 1030-1100 cm^{-1} (Si-O-Si) among other bands. The NMR spectrum (CCl_4) showed multiplets centered at 7.40 δ ($Si-C_6H_5$), and 0.75 δ ($-CH_2-CH_2-$) and a doublet at 0.20 δ ($CH_3-Si-CH_3$).

5. Polymerization of Cyclic E

The polymerization of cyclic E was conducted exactly as described for cyclic D except the reaction time was 4 hours. The polymerization reaction was quenched by means of a drop of glacial acetic acid and the polymer precipitated in methanol and dried. The infrared spectrum showed bands at 3000-3100 cm^{-1} (CH, aromatic), 2860-2960 cm^{-1} (C-H, aliphatic), 1580 cm^{-1} (C=C), 1120 cm^{-1} ($Si-C_6H_5$), 1255 cm^{-1} ($Si-CH_3$) and 1030-1100 cm^{-1} (Si-O-Si) among other bands. The NMR spectrum (CCl_4) showed multiplets centered at 7.50 δ ($Si-C_6H_5$) and 1.00 δ ($-CH_2CH_2-$) and a singlet at 0.20 δ ($Si-CH_3$).

6. Polymerization of Cyclic F

The polymerization of cyclic F was conducted as described for cyclic A. The solution turned turbid after 2 hours and the polymer formed precipitated out of the solution as a white powder. The solution was stirred for 24 hours and the precipitated polymer was filtered and dried. The polymer was insoluble in aliphatic hydrocarbons, aromatic hydrocarbons, THF, DMSO, diphenylether etc. The infrared spectrum (KBr pellet; 10% conc.) showed bands at 3000-3100 cm^{-1} (C-H, aromatic), 2860-2960 cm^{-1} (C-H, aliphatic), 1580 cm^{-1} (C=C), 1160 cm^{-1} (SiC_6H_5) and 1020-1140 cm^{-1} (Si-O-Si) among other bands.

F. THE PREPARATION OF INITIATOR

The initiator used in this work was lithium n-butyldiphenylsilanolate and was prepared by reacting hexaphenylcyclotrisiloxane (trimer) with n-butyllithium. The reaction of n-butyllithium with trimers was found to be quantitative[43]. Lithium silanolates prepared by the above method have been used[44] as initiators without their isolation.

1. The Preparation of Hexaphenylcyclotrisiloxane (Trimer)

The trimer was prepared according to the method of Takiguchi[45]. A solution of 150 g (0.6 mole) diphenyldichlorosilane in 300 ml methyl acetate was added dropwise, while stirring mechanically, to 72 g (0.9 mole) of zinc oxide (dried in an oven at 100° for 24 hours) and 600 ml methyl acetate in a 2 liter 3-necked flask. After the addition of chlorosilane, the mixture was stirred for another 15 minutes under gentle reflux. The silicone-containing products were dissolved in 600 ml benzene and the resulting mixture was washed in portions with water in a 2 liter separatory funnel to remove zinc chloride. Washing

with water was continued until the aqueous extract was neutral. To the organic layer, 600 ml of ethanol was added and the liquid evaporated to dryness in a hood. The white mass mixed with oily liquid was recrystallized out as white plates (35 g, 30%, mp 189.3° lit.[45] 97%, mp 188-190°). The very high yields reported in the literature were not obtained.

2. Analysis of n-Butyllithium

n-Butyllithium was obtained from Alfa Inorganics as a 2.28 M solution in hexane. Since the reaction of n-butyllithium with the trimer is quantitative, it was necessary to analyze the n-butyllithium solution and obtain its concentration.

The analysis of n-butyllithium was carried out according to the double titration method outlined by Gilman[46]. The method involves titrations to find the total alkali content in n-butyllithium solution and the alkali content due to hydrolyzed n-butyllithium (if any). Substraction of the latter value from the former yields the alkali content due to n-butyllithium only.

a. Apparatus

All glassware used in the analysis was baked for 24 hours in an oven at about 200°, and flushed with argon while being cooled. The argon was dried by passing it through a trap (supplied by Guild Corporation) containing active charcoal, indicating molecular sieves (type 13X) and non-indicating molecular sieves (type 13X). All reactions except the titration were carried out inside a polyethylene glove bag filled with argon.

b. Reagents

Anhydrous ether was distilled from lithium aluminum hydride;

1,2-dibromoethane was maintained dry by storing over phosphorous pentoxide. The standard acid used in this titration was prepared by dissolving 12.8300 g of potassium biphthalate crystals (FW 204.3 g) in 250 ml water in a volumetric flask, thereby obtaining a 0.2512 M solution.

c. Total alkali content in n-butyllithium

The total alkali content in n-butyllithium was determined by pipeting 5.0 ml of n-butyllithium solution into 10 ml of ether in a 250 ml Erlenmeyer flask. To this solution 10 ml of distilled water was added and the contents shaken well. Manipulations up to this time were conducted inside the glove bag.

The Erlenmeyer flask was taken out of the glove bag, a drop of phenolphthalien indicator was added and the solution titrated against 0.2112 M standard acid. Duplicate titer was 47.0 ml.

d. Hydrolyzed alkali content in n-butyllithium

The amount of alkali due to hydrolyzed n-butyllithium was determined by pipeting 5.0 ml of n-butyllithium in 10 ml ether in an Erlenmeyer flask. To this solution 3 ml of 1,2-dibromoethane was added and the solution shaken well. The bromo compound reacts with n-butyllithium converting it into lithium bromide, whereas the hydrolyzed alkali is unreactive to it. The solution was taken out of the glove bag and about 10 ml of distilled water was added. The contents were shaken well, and titrated against 0.2512 M acid. Duplicate titer was 2.3 ml.

From the above analyses the amount of alkali, present as n-butyllithium only, in 5 ml of original solution = (47.0 - 2.3) ml of 0.2512 M acid solution. Therefore the concentration of n-butyllithium

solution was 2.246 M.

3. The Reaction of n-Butyllithium with Hexaphenylcyclotrisiloxane

The reaction was carried out in a dry argon atmosphere inside a polyethylene glove bag. A solution of 5.94 g (0.01 mole) of trimer in 100 ml of dry benzene was taken in a dry 200 ml, 3-necked flask fitted with a magnetic stirrer. By means of a hypodermic syringe, 13.5 ml (0.03 mole) of 2.246 M n-butyllithium solution in hexane was added dropwise with stirring. Upon addition a mild exothermic reaction was noted. After the addition of n-butyllithium, the mixture was stirred for 10 more minutes, and the solvents evaporated under a vigorous flow of argon to give a white salt. The salt was redissolved in 100 ml dry benzene and stored under argon in a dry, tightly capped volumetric flask.

The initiator was identified by hydrolyzing 5 ml of the initiator solution in 5 ml distilled water. To the heterogeneous solution 10 ml of diethylether was added and the aqueous layer separated in a separatory funnel. The organic layer was washed with distilled water to remove any lithium hydroxide. The organic layer was transferred to a crystallizing dish and the solvents evaporated when a white waxy substance was obtained. This was dried in a vacuum oven for 48 hours at 40^{o}. The infrared spectrum (KBr pellet; 10% conc.) showed among other bands a strong absorption band at 3200-3500 cm^{-1} (Si-OH). The NMR spectrum (CCl_4) had multiplets centered at 7.30 δ (10H, Si-C_6H_5) and 1.05 δ (9H, Si-C_4H_9) and a singlet at 3.86 δ (1H, Si-OH). Thus it was identified that the derivative obtained from the hydrolysis of the initiator was n-butyldiphenylsilanol, and hence the initiator was lithium n-butyldiphenylsilanolate.

4. Analysis of the Initiator Solution

The analysis of the initiator solution was conducted by pipeting 5.0 ml of the initiator solution into a 250 ml Erlenmeyer flask and about 10 ml of distilled water was added. The solution was shaken well and allowed to stand for 5 minutes. A drop of phenolphthalien indicator was added and the solution titrated against 0.0984 M potassium biphthalate solution, (prepared by dissolving 5.0262 g of the salt in 250 ml distilled water in a volumetric flask). Vigorous shaking near the end point was required because of the heterogeneous nature of the solution. Duplicate titer was 15.3 ml, and from this the molarity of the initiator solution was determined to be 0.3 M.

All reaction rate studies were made with aliquots taken from 0.14 M stock solution. This solution was prepared by diluting 20.0 ml of 0.3 M initiator with 23.0 ml dry benzene in a dry 50 ml volumetric flask. The molarity was again checked by titration. In order to see if there was any n-butyllithium left unreacted in the solution, Gilman's[44] procedure was followed once again by shaking 5 ml of the initiator solution with about 3 ml of 1,2-dibromoethane in an argon atmosphere, hydrolyzing with about 10 ml distilled water and then titrating against standard acid. The same molarity was obtained indicating there was no unreacted n-butyllithium present in the solution, and all the alkali content was due to lithium n-butyldiphenylsilanolate salt.

G. DETERMINATION OF REACTION RATES

1. Materials

a. Monomers

All the monomers except monomer F were distilled before kinetics measurements were started.

b. Solvent

Benzene (certified ACS grade) was redistilled twice from lithium aluminum hydride and stored over fresh 4Å molecular sieves in an amber colored bottle. The water content in benzene after storing over molecular sieves for several days was about 30 ppm as determined by Karl-Fischer titration.

c. Promoter

Tetrahydrofuran (THF) was used as a promoter. THF was redistilled twice from lithium aluminum hydride and stored under argon over fresh molecular sieves in an amber colored bottle. The water content in THF was about 45 ppm as determined by Karl-Fischer titration.

d. Initiator

The initiator used was lithium n-butyldiphenylsilanolate, as a 0.14 M solution in benzene. All additions of monomer, solvent, promoter and initiator were performed by means of micro syringes.

2. Calibration of 500 μl Syringe with Monomers

In order to add exactly the same amount of monomer for various kinetic runs, the 500 μl syringe with 10 μl calibration markings was calibrated with each monomer to obtain $1.25 - 1.28 \times 10^{-3}$ mole of each monomer. This variation was due to limitations inherent in the syringe technique and also due to viscosities of the monomers.

3. Reaction Rate Studies at 31.7°

The rates of polymerization of the monomers were studied by obtaining conversion data with respect to time inside the probe of a Varian EM 360 NMR spectrometer. The use of NMR spectrometry for

obtaining conversion data was possible because of different chemical shifts of the protons under investigation for the cyclic monomer and the polymer formed.

All reaction rate studies were made at 31.7°, the temperature of the NMR tube in the probe. The temperature was determined by spinning an NMR tube with about 1 ml Dow Corning 200 fluid for about 30 minutes, the tube taken out and the temperature measured immediately by a copper-constantan thermocouple. The temperature of the magnet and hence the probe was controlled by a proportional type controller and was kept constant.

All studies of the effect of variables upon rate, such as the effect of varying the promoter concentration at a constant initiator concentration, effect of varying the initiator concentration at a constant promoter concentration was conducted only on cyclic A. From this study a set of conditions was chosen which was maintained constant for all other cyclic polymerization.

The experimental procedure consisted of measuring from a calibrated syringe the required amounts of monomer, solvent and promoter into a dry NMR tube. The solution was mixed and thermostated by spinning the tube for about 10 minutes. The NMR tube was taken out of the probe and the initiator solution added. Immediately an electric timer capable of reading at 0.1 second was started. After mixing the components, the NMR tube was placed inside the probe. The monomer and the polymer peaks were scanned at 2ppm sweep width and electronically integrated noting the time of integration. Integration of the peaks yielded the relative amounts of monomer that remained unreacted

and the amount of polymer formed. From this the percent conversion was calculated.

4. Reaction Rate Studies at 20^{o} and 40^{o}

The effect of temperature on the polymerization rates of the cyclics was obtained by carrying out the polymerization at $20^{o} \pm 0.1^{o}$ and $40^{o} \pm 0.1^{o}$ in a constant temperature bath. These measurements were made on cyclics A, B, C and E.

The experimental procedure consisted of syringing out the proper amounts of monomer, benzene and THF in a dry NMR tube, mixing and thermostating for 15 minutes before the initiator was added. Immediately the electric timer was started and at a certain time a drop of glacial acetic acid was added to quench the reaction. The NMR tube was taken out of the constant temperature bath, the tube wiped dry and the percent conversion obtained by integrating the monomer and polymer peaks. The fact that acetic acid quenches the polymerization reaction was checked by repeatedly integrating the monomer and polymer peaks over a period of 24 hours. No change in the percent conversion was seen. Thus by carrying out a series of eight runs and quenching at different times a complete set of conversion data at the desired temperature was obtained.

H. CHARACTERIZATION OF POLYMERS

1. Determination of Molecular Weights and Molecular Weight Distribution

Molecular weights and molecular weight distribution were obtained by means of gel permeation chromatography (GPC) analyses using a Waters Ana-Prep Gel Permeation Chromatograph fitted with columns packed with Corning controlled porosity glass and "PORASIL"

(1500, 370, 240 and 125 Å). The column sets were calibrated with a series of narrow molecular weight distribution polystyrene standards. A calibration curve was constructed by plotting the peak molecular weight against elution volume.

All GPC analyses on the polymers were performed with a THF flow rate of about 1 ml/min. The experimental procedure consisted of quenching the polymerization reaction at the end of a kinetic run with a drop of glacial acetic acid, evaporating the solvents and injecting into the instrument 2 ml of approximately 0.125-0.25% solution of the polymer in THF. From the GPC chromatograms the molecular weight and the molecular weight distribution were obtained.

IV. RESULTS AND DISCUSSION

A. PREPARATION OF MONOMERS

The reactions leading to the monomers are well-known and no particular difficulty was encountered in the preparation of monomers. Many of the chlorosilanes used were prepared by Grignard synthesis and the use of phenylmagnesium chloride in THF was found to give better yields in the preparation of vinylchlorosilanes. Details of these syntheses pertinent to the final results follow.

1. Grignard Synthesis

Phenylmethylvinylchlorosilane was prepared by Grignard reaction between methylvinyldichlorosilane and phenylmagnesium chloride in THF. The use of THF as the solvent enabled the use of higher temperatures (65^{o}) and hence shorter reaction times (8 hours as opposed to 22 hours using ether as the solvent). Further, the yield of phenylmethylvinylchlorosilane in THF media was 67% as compared to 41% using phenylmagnesium chloride in ether.[40]

In the preparation of diphenylvinylchlorosilane a two step Grignard synthesis was utilized. Phenylvinyldichlorosilane was first prepared (in 52% yields) by reacting 1 mole of vinyltrichlorosilane with 1 mole of phenylmagnesium chloride in the THF at ambient temperature. Subsequent reaction of 1 mole of phenylvinyldichlorosilane with 1 mole of phenylmagnesium chloride in THF yielded diphenylvinylchlorosilane in 44% yields (22% overall yield). Attempts to prepare diphenylvinylchlorosilane by reacting 1 mole of vinyltrichlorosilane with 2 moles phenylmagnesium bromide in ether resulted in poor yields

(10-15%) of diphenylchlorosilane. Curry[40] also reported that Grignard reaction involving 1 mole of vinyltrichlorosilane with 2 moles phenylmagnesium chloride in ether resulted in unfavorable product distribution.

2. The Exchange of Chloro and Ethoxy Groups Upon the Addition of Dimethylchlorosilane to Vinyldimethylethoxysilane

In the hydrosilation addition reaction used in the preparation of cyclic A, dimethylchlorosilane and vinyldimethylethoxysilane were utilized. It was expected that in the presence of chloroplatinic acid the addition of dimethylchlorosilane to vinyldimethylethoxysilane would go smoothly to give the adduct 1-(dimethylchlorosilyl)-2-(dimethylethoxysilyl)ethane (I) as shown below.

$$ClSi(Me)_2H + CH_2{=}CHSi(Me)_2OEt \xrightarrow[H_2PtCl_6\cdot 6H_2O]{} ClSi(Me)_2CH_2CH_2Si(Me)_2OEt \quad (I)$$

However fractionation of the hydrosilation adduct yielded in addition to (I) two other adducts 1,2-bis(dimethylchlorosilyl)ethane and 1,2-bis(dimethylethoxysilyl)ethane. The formation of these adducts is explained on the basis of chloro and ethoxy exchange reactions among the reactants and products (Appendix B).

B. EFFECT OF RING STRAIN ON POLYMERIZATION

The 5-membered cyclocarbosiloxanes were found to be strained and the strain energy was estimated[7] to be 8-12 kcal/mole for the cyclics A through F. This is also evident in the infrared absorption frequency of the Si-O-Si bond in the cyclic monomers and the linear polymers. The absorption frequency of the Si-O-Si bonds measured on the cyclic monomers and the linear polymers are listed in Table II.

TABLE II

INFRARED ABSORPTION FREQUENCIES OF Si-O-Si BONDS
IN THE CYCLIC MONOMERS AND THE LINEAR POLYMERS

Cyclic Monomer	Wave Number cm^{-1} (monomer)	Wave Number cm^{-1} (polymer)
A	924	1050-1080
B	920	1050-1090
C	915	1030-1100
D	920	1030-1100
E	915	1030-1100
F	910	1020-1140

The Si-O-Si bands are broadened in the polymers.

An inspection of Table II shows that in going from the monomer to the polymer the absorption frequency of the Si-O-Si bond is shifted to higher wavenumbers. This large shift in the Si-O-Si stretching frequency in the polymer is attributed[7] to relief of ring strain upon ring-opening. Table II also shows among the monomer series itself strain in the ring is increased by phenyl substitution as evidenced by a change in absorbance from 924 to 910 cm^{-1}. If the phenyl groups are sterically crowded such as in cyclic C, E or F, the Si-O-Si bond angle is changed to accommodate the phenyl groups, increasing the strain in the rings.

The relief of ring strain upon polymerization is also manifested in the NMR spectrum of the monomers and the polymers derived from them.

The chemical shifts of the protons under observation are shifted upfield in the polymers compared to the monomers.

The chemical shifts of the protons under observation for the monomers and the polymers are listed in Table III.

TABLE III

CHEMICAL SHIFTS IN NMR SPECTRA
OF THE MONOMERS AND POLYMERS

Cyclic Monomer	Proton Observed	Chemical Shifts Monomer δ	Polymer δ
A	CH_2-CH_2	0.68	0.40 (singlet)
B	$Si(CH_3)_2$	0.20	0.10 (doublet)
C	$Si(CH_3)$	0.45	0.22 (singlet)
D	$Si(CH_3)_2$	0.50	0.20 (doublet)
E	$Si(CH_3)$	0.55	0.20 (singlet)
F	CH_2-CH_2	1.32	---

The chemical shifts reported here were obtained separately on approximately 15 wt% solution of the monomers and the polymers in carbontetrachloride. Adequate separation between the monomer and the polymer peaks was obtained at 2 ppm sweep width permitting electronic integration of the two peaks.

C. DETERMINATION OF REACTION RATES

Since the chemical shifts of the protons of the monomer and the polymer are different, it was possible to study the rate of polymerization of the monomers by obtaining conversion data with respect to

time in an NMR spectrometer. The advantage of this method over the conventional quenching and weighing method for determining the amount of polymer formed or gas-liquid chromatography for determining the amount of unreacted monomer is based on the fact that conversion data can be obtained without any sample withdrawal.

A portion of the NMR spectra obtained during the polymerization of cyclic A is shown in Figure 1. It shows, at a reaction time of 5 minutes, the monomer as the larger peak and the polymer as the smaller peak (12.4% conversion). The spectra gradually changes so that at 40 minutes it shows the monomer as the smaller peak and the polymer as the larger peak (93.0% conversion).

The reaction rate studies will be considered in the following parts.

(1) The effect of varying the concentration of THF upon the rate of polymerization of cyclic A at a constant initiator concentration.

(2) The effect of varying the concentration of THF upon the molecular weight and the molecular weight distribution.

(3) The effect of varying the concentration of the initiator upon the rate of polymerization of cyclic A at a constant THF concentration.

(4) The effect of varying the initiator concentration upon the molecular weight and the molecular weight distribution.

(5) The effect of water concentration upon the rate of polymerization of cyclic A.

(6) The effect of water concentration upon the molecular weight and the molecular weight distribution.

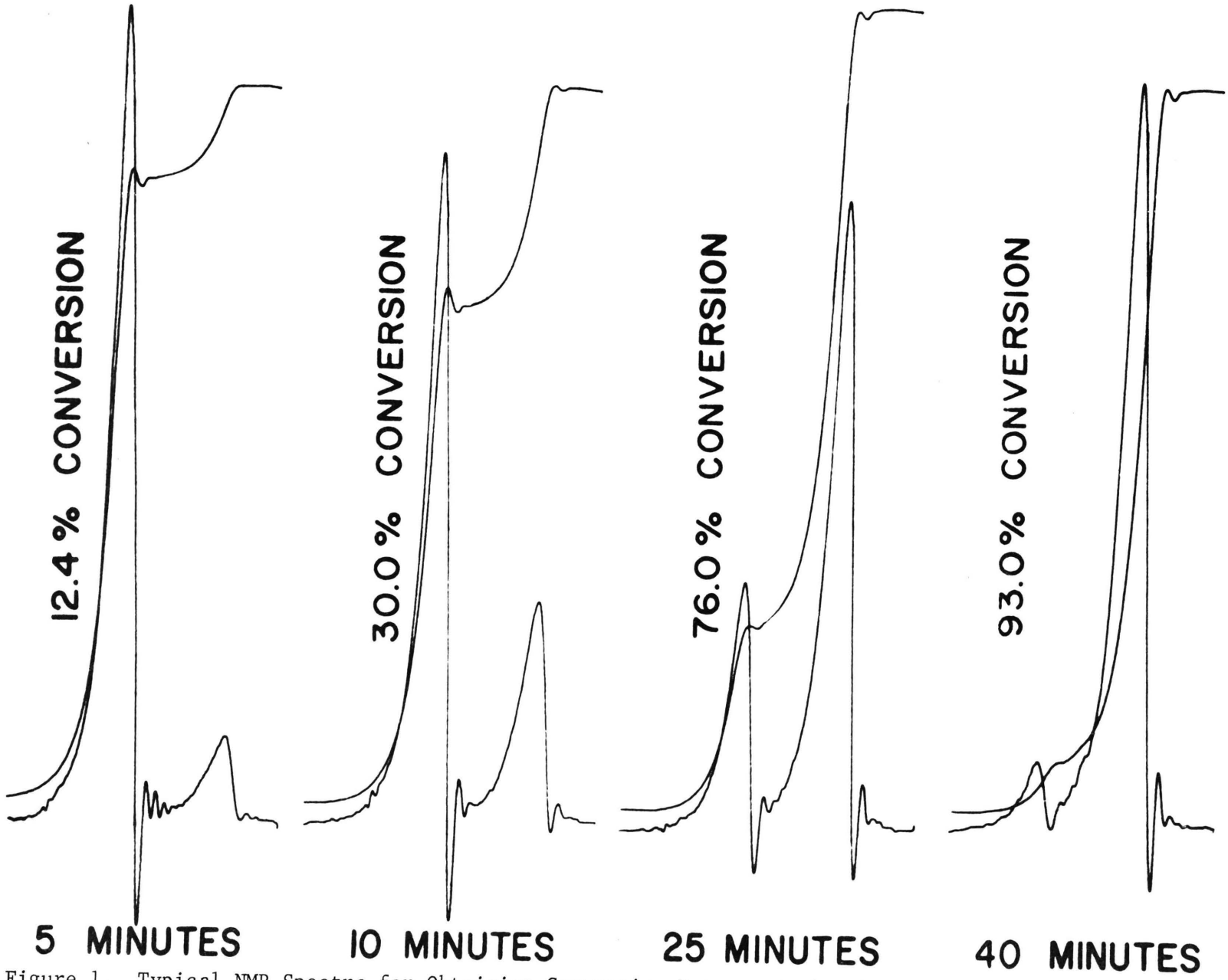


Figure 1. Typical NMR Spectra for Obtaining Conversion Data on Cyclic A

(7) The effect of substituting phenyl groups for methyl groups upon the rate of polymerization of cyclic monomers.

(8) Reaction rate studies on the polymerization of cyclics B, C, D, E and F.

(9) The effect of temperature upon the rate of polymerization of the cyclic monomers.

Before discussing the effect of the above variables, the amount of water introduced into the system through solvent, promoter and monomer requires elucidation. Benzene (used as a non-reactive solvent) and THF (used as promoter) were distilled twice from lithium aluminum hydride and stored over fresh $4A^{o}$ molecular sieves. The equilibrium water content in benzene was < 30 ppm and in THF was < 45 ppm. An attempt was made to determine the water content in cyclic A by Karl-Fischer titration. The titration proceeded without any endpoint even after appreciable quantities of Karl-Fischer reagent was added. This behavior suggests that the Karl-Fischer reagent opened the cyclic A presumably forming $HOSi(CH_3)_2CH_2CH_2Si\text{-}(CH_3)_2SO_3H$ due to the SO_3 present in the reagent and the -SiOH formed titrated against the Karl-Fischer reagent. Therefore the water content in the monomer could not be determined, but was constant throughout this work.

The water concentration introduced into the system from benzene and THF alone is illustrated by the following example.

The concentration of components in the reaction mixtures used, while studying the effect of THF as a variable, were as follows:

[Initiator] = 3.0×10^{-3} mole/liter

[Monomer] = 1.073 mole/liter

[Benzene[= 7.263 - 8.378 mole/liter

[THF] = 0.2137 - 1.574 mole/liter

[Water] = 1.2×10^{-3} mole/liter (from solvents)

The amount of water introduced by benzene, on an average, was 1.0×10^{-3} mole/liter, and that introduced by THF was 0.2×10^{-3} mole/liter so that the total amount of water introduced by benzene and THF alone was 1.2×10^{-3} mole/liter. Thus the concentration of water is comparable to that of the initiator.

Throughout this work whenever it is stated that one variable is kept constant while the other is varied, it is also implied that the water concentration remains constant for a given set of reaction parameters. In section 5 it will be shown that the water concentration does not greatly affect the rate of polymerization but it does alter the molecular weight and the molecular weight distribution significantly.

1. The Effect of THF Concentration Upon the Rate of Polymerization of Cyclic A

The percentage conversion of monomer to polymer, as a function of time at various concentrations of THF obtained at 31.7° and at a constant initiator concentration of 3.0×10^{-3} mole/liter, is shown in Figure 2. The rate of polymerization increased with increasing concentration of THF at a constant initiator concentration. The percentage conversion of monomer to polymer is shown as a first order plot in Figure 3, and the rate constants calculated from these data are plotted logarithmically with respect to the concentration of THF

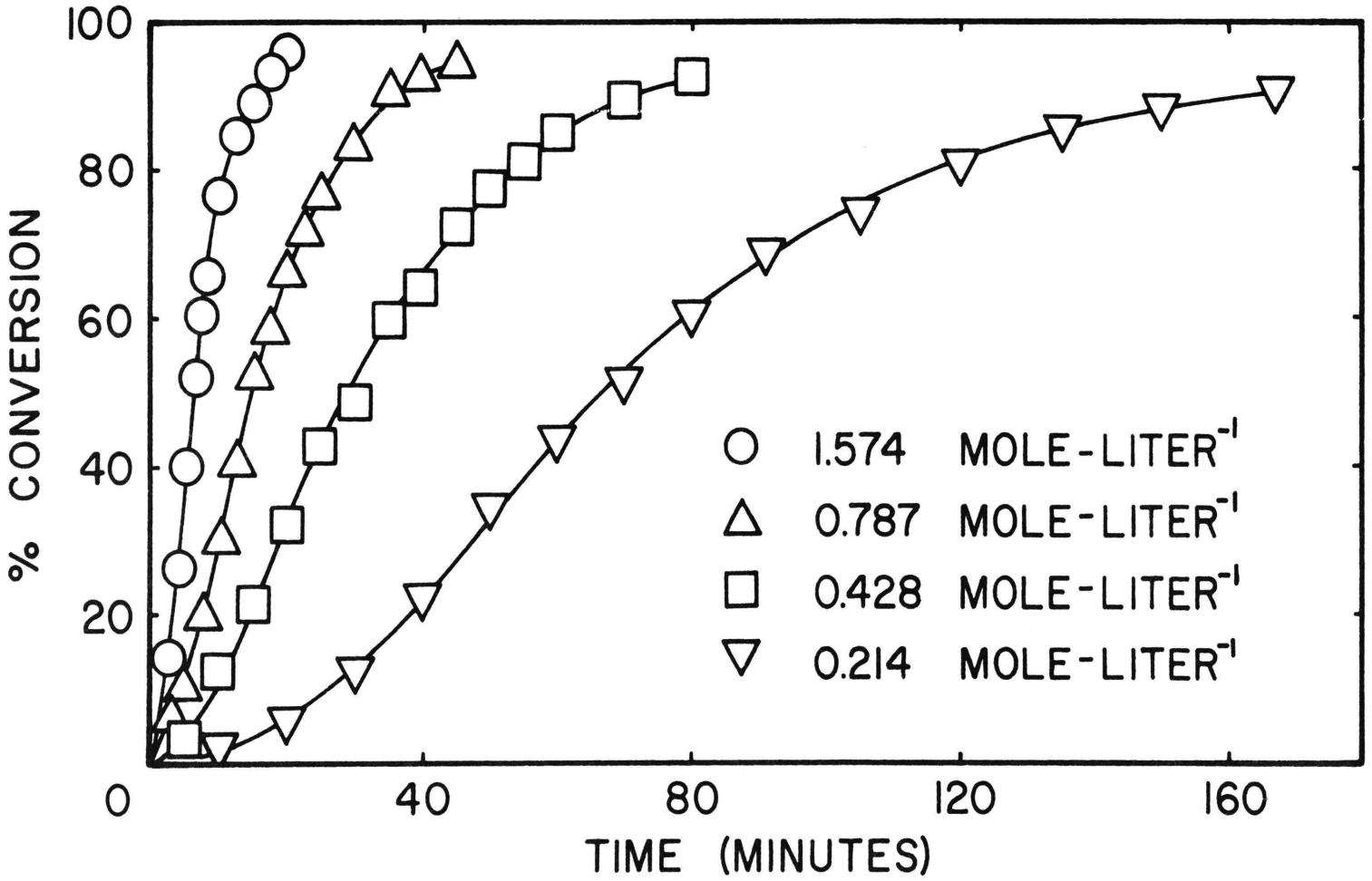


Figure 2. Conversion Data for the Polymerization of Cyclic A as a Function of THF Concentration

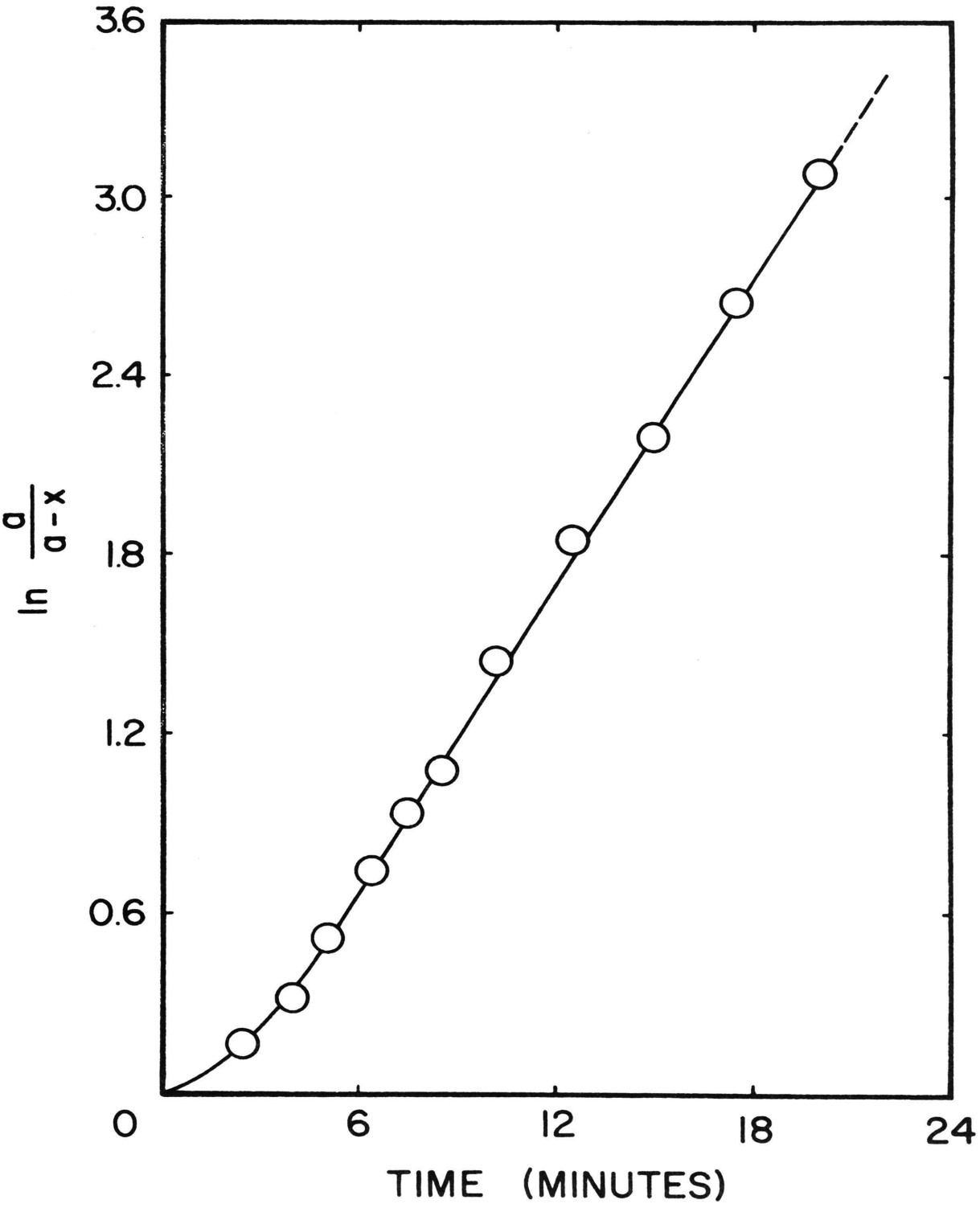


Figure 3. First Order Plot for Polymerization of Cyclic A at 31.7° and at Concentrations of Initiator 3.0×10^{-3} Mole/Liter and THF 1.574 Mole/Liter

in Figure 4. The effect of THF concentration on the rate of polymerization of A is discussed below.

Ionization of the initiator in the absence of a promoter yields an intimate or contact ion-pair in which the cation and anion lie in a common solvation shell. Such a situation exists in hydrocarbon solvents. In the presence of THF, the contact ion-pairs are transformed to solvated ion-pairs in which the cation and anion occupy different solvation shells. Evidence for the existence of solvated ion-pairs was shown recently by Juliano et al.[42]. They utilized lithium n-butyldimethylsilanolate as a model compound. The NMR spectrum of the compound in hydrocarbon media, such as toluene/hexane in which it existed as contact ion-pairs, showed silicon methyl proton signals at 9.97 τ. When THF was added, there appeared another resonance signal at 10.05 τ which was ascribed by them to the THF solvated lithium n-butyldimethylsilanolate. This upfield shift from the contact ion-pair was explained as a charge separation effect. Solvation of the lithium counter-ion by THF produced a greater charge separation of the salt, hence a greater shielding of the silicon methyl protons. Further, the ratio of solvated ion-pair to contact ion-pair depended on the amount of THF added, increasing with increasing THF amount.

The increase in rate of polymerization of A with increasing concentration of THF at a constant concentration of initiator can be explained using the "ion-pair" concept. Increasing the concentration of THF produces more solvated ion-pairs which are the active species in causing ring-opening reaction. In order to verify this, an experiment was conducted in which no THF was added. No polymerization was

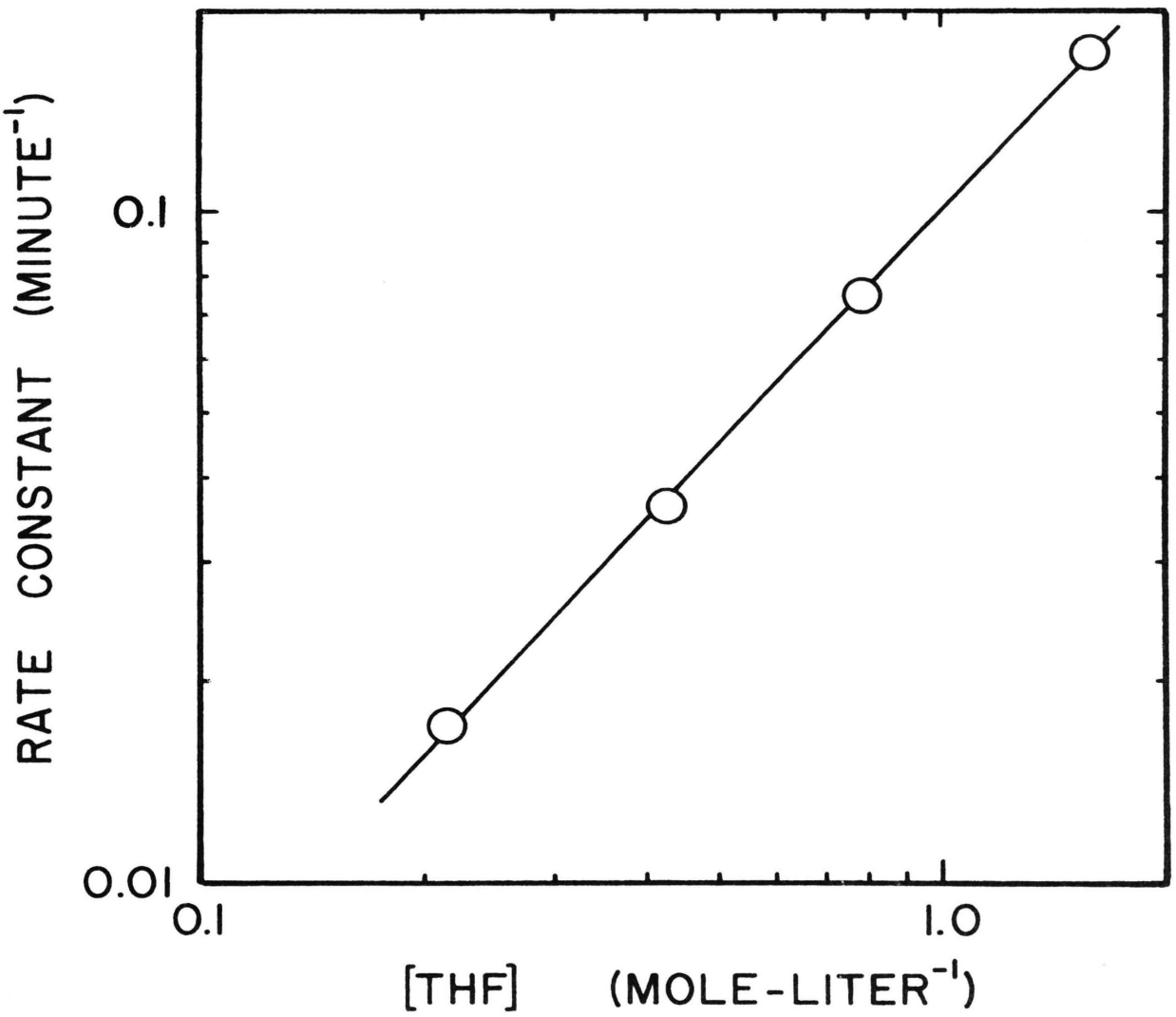


Figure 4. Rate of Polymerization of Cyclic A as a Function of THF Concentration

noticed even after 20 hours at 31.7°. Thus it was established that the contact ion-pair is inactive in initiating the polymerization reaction.

The slope of the logarithmic plot Figure 4 is an indication of the effectiveness of the promoter. Increasing slopes indicate better solvating power of the promoter. In this study the slope is unity for THF. It is known[47] that hexamethylphosphoramide (HMPA) has a much higher solvating power than THF and should polymerize A faster than did THF at a given promoter level. This was checked qualitatively by carrying out the polymerization of A under the same conditions as with THF. While it took nearly 3 hours for 90% conversion with THF, the same conversion was attained with HMPA in approximately 5 minutes clearly indicating its greater solvating power.

The THF promoted system displayed an induction period, at a constant initiator concentration of 3.0×10^{-3} mole/liter, which decreased with increasing THF concentration. These data are presented in Table IV.

TABLE IV

INDUCTION PERIODS DURING THE POLYMERIZATION OF CYCLIC A

[THF]	Induction Period Minutes
0.214	34.0
0.428	17.0
0.787	8.0
1.574	3.4

This behavior, as explained by Ostrozynski[25], suggests that the equilibrium population of solvated active ends is not attained spontaneously but rather their formation proceeds at a finite rate. This step governs the initial stages of polymerization where it displays an induction period.

2. The Effect of THF Concentration Upon the Molecular Weight and the Molecular Weight Distribution

The GPC chromatograms of the polymers, obtained upon polymerization at a constant initiator concentration of 3.0×10^{-3} mole/liter and varying THF concentration, showed a bimodal distribution with the peak molecular weight of the high molecular weight fraction exactly twice the peak molecular weight of the low molecular weight fraction. This behavior as explained by Lee[48] is due to the amount of water present in the system. The reactions responsible for the formation of polymers having bimodal distribution can be summarized as follows.

$$Ph_2BuSiO(Me_2SiCH_2CH_2SiMe_2O)_xLi + H_2O \rightleftharpoons$$

(I)

$$Ph_2BuSiO(Me_2SiCH_2CH_2SiMe_2O)_xOH + LiOH$$

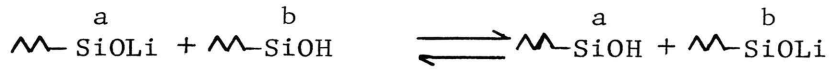
(I')

where x = 0,1,2,3 . . . . . .

$$LiOH + Me_2\overline{SiCH_2CH_2SiMe_2O} \longrightarrow$$

$$LiOMe_2SiCH_2CH_2SiMe_2OH$$

(II)



growing chain chain temporarily terminated

a & b represent Si on different chains

The exchange reaction shown above is very fast. Thus the monofunctional polymer (I and I') and the difunctional polymer (II) all have equal probabilities to grow and the chain length of the difunctional polymer will be twice that of the monofunctional polymer. Therefore the resulting polymer has a bimodal distribution.

The areas of the GPC chromatograms obtained in this study were measured by planimetry. Assuming curves to be described by a Gaussian distribution, the peak molecular weights and their relative areas were obtained. Table V shows the case of varying THF concentration at a constant initiator concentration of 3.0×10^{-3} mole/liter.

It is seen from Table V that the weighted peak molecular weight, M_p did not change appreciably. The rate, however, increased by a factor of 10 while going from lowest to highest THF concentration. This is expected since keeping the initiator and monomer concentrations constant results in the same number of growing species resulting in the same average molecular weight, but the solvation of the active species is increased when the THF concentration is increased resulting in an increased rate of polymerization.

3. The Effect of Initiator Concentration Upon the Rate of Polymerization of Cyclic A

The effect of varying the initiator concentration upon the rate of polymerization of A at constant THF concentrations is shown in

TABLE V

PEAK MOLECULAR WEIGHTS AND THEIR RELATIVE AREAS
AS A FUNCTION OF THF CONCENTRATION
AT A CONSTANT INITIATOR CONCENTRATION[a]

[THF]	$\frac{[\text{Initiator}]}{[H_2O]}$	Peak Molecular Weight M_{p_1}	% Area	Peak Molecular Weight M_{p_2}	% Area	Weighted M_p
0.214	2.68	34,000	40	68,000	60	54,400
0.428	2.52	31,000	35	62,000	65	51,100
0.787	2.42	36,000	44	72,000	56	53,200
1.574	2.23	36,000	40	72,000	60	57,600

[a]In benzene at 31.7°

Figure 5. The rate of polymerization is directly proportional to the square root of initiator concentration at low initiator concentrations. It reaches an asymptotic value at a certain initiator concentration. This behavior is explained on the basis of the formation of contact and solvated ion-pairs.

$$\underset{\text{unionized salt}}{\equiv SiOLi} \overset{I}{\rightleftharpoons} \underset{\text{contact ion-pair}}{\equiv SiO^{(-)},Li^{(+)}} \overset{II}{\underset{THF}{\rightleftharpoons}} \underset{\text{solvated ion-pair}}{\overset{-}{\underset{-}{\equiv}} SiO^{(-)}, (THF)_nLi^{(+)}}$$

Increasing the initiator concentration beyond the levels at which an asymptotic value in rate is reached results in increased amounts of contact ion-pairs in the ionic equilibrium I. However, the concentration of THF remains the same with the result the degree of solvation of the lithium counterions is reduced. Increasing the initiator concentration also results in an increase in the number of growing chains as evidenced by a decrease in the molecular weight. Therefore, the decrease in the activity of the ion-pairs by lesser solvation is offset by the increase in the number of growing chains with the result an asymptotic value in rate is reached.

Decreasing the initiator concentration below the concentration levels at which the asymptotic value is reached results in a decrease in rate. This is due to a decrease in the formation of contact ion-pairs in the ionic equilibrium I, which at the same concentration of THF is converted to solvated ion-pairs. In this case it is proposed that the equilibrium II is completely shifted towards solvated ion-pairs. Juliano[49] found that the amount of solvated ion-pairs depended on the

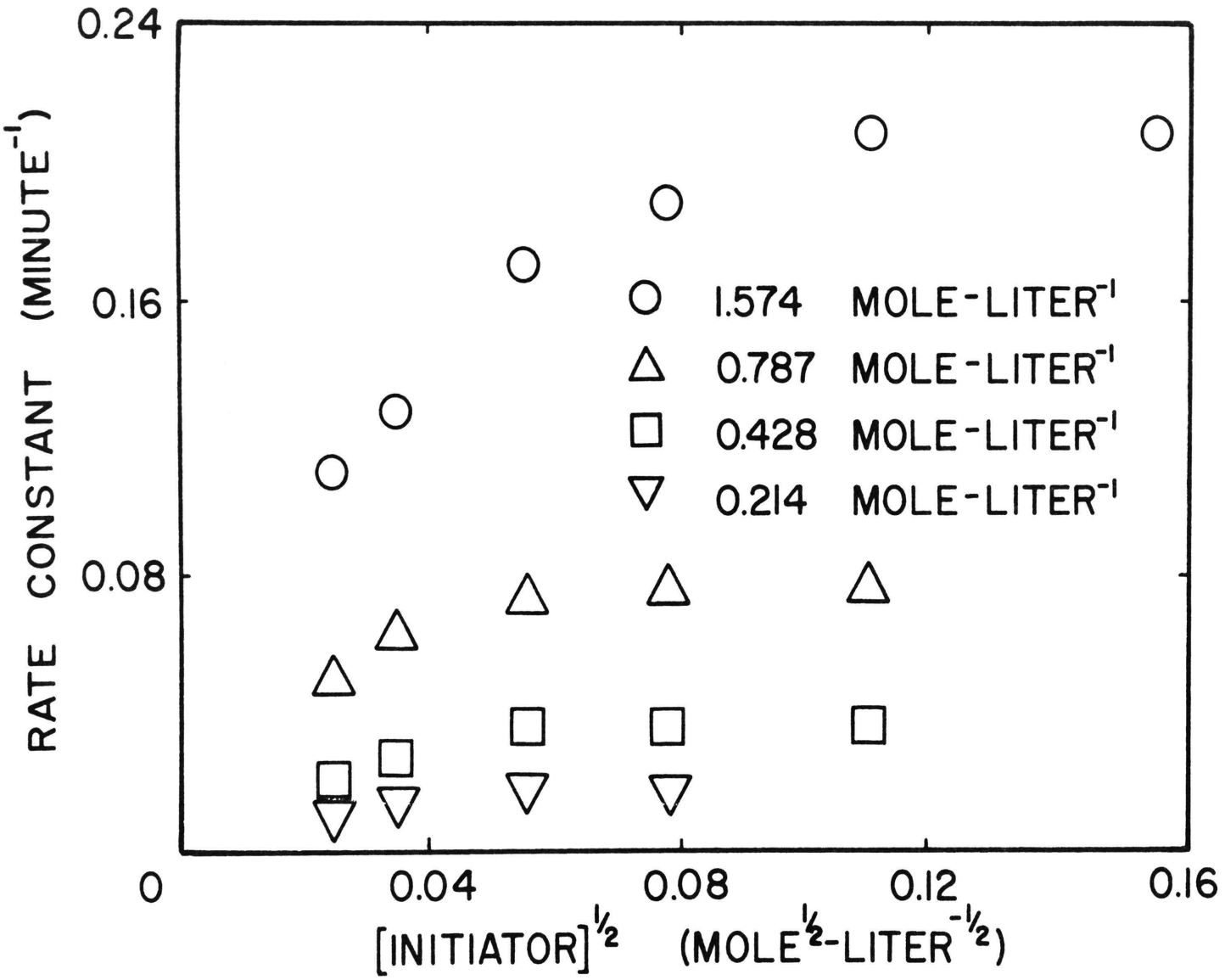


Figure 5. Rate of Polymerization of Cyclic A as a Function of Initiator Concentration

concentration of THF present. At low initiator concentrations all of the contact ion-pairs formed will be converted to solvated ion-pairs. Therefore only equilibrium I is important in determining the number of contact ion-pairs formed.

For equilibrium I the equilibrium constant

$$Ke_I = \frac{[\equiv SiO^{(-)}][Li^{(+)}]}{[\equiv SiOLi]}$$

Since $[\equiv SiO^{(-)}] = [Li^{(+)}]$, Ke_I can be expressed as

$$Ke_I = \frac{[\equiv SiO^{(-)}]^2}{[SiOLi]} \quad \text{or} \quad [\equiv SiO^{(-)}] = Ke_I^{\frac{1}{2}}[\equiv SiOLi]^{\frac{1}{2}}$$

Since the propagation rate constant k_p is directly proportional to the concentration of silanolate anion $[\equiv SiO^{(-)}]$, the observed rate constant would be expected to be directly proportional to the square root of the initiator concentration. The square root dependency was observed in this work and also by Morton and Bostick[27] during the polymerization of octamethylcyclotetrasiloxane initiated by potassium naphthalene complex in THF solution. They used 50 vol % of monomer solution in THF, and the molecular weights obtained were in the range 10^6 indicating a very low initiator concentration. Thus their results agree with the results obtained in this study at low initiator concentrations. However Morton and Bostick[27] did not vary the initiator concentration over a sufficiently wide range to observe the asymptotic behavior.

Yuzhelevskii and his coworkers[30] studied the anionic polymerization of 2,4,6-tris(3,3,3-triflurorpropyl)-2,4,6-trimethylcyclotrisiloxane, $[CH_3Si(CH_2CH_2CF_3)O]_3$, using sodium silanolate as an initiator

and dimethylformamide as an activator. They reported that increasing the activator concentration increased the rate at a constant initiator concentration. However they found that when the initiator concentration was varied at a constant activator concentration, plots of rate constant versus initiator concentration (logarithmic) exhibited curves having a maxima, after which the polymerization rate decreased with increase in initiator concentration over a wide range of concentrations. The explanation offered was that when the initiator concentration was varied, (starting at a specific level) there was insufficient free activator molecules relative to the number of initiator molecules with the result that there was a transition from the more highly solvated to less highly solvated ion-pairs. Thus despite the increase in the total number of growing centers, their activity decreased because they were less highly solvated and the overall rate of polymerization was reduced.

In this study when the initiator concentration was varied at a constant promoter concentration, the polymerization rate reached an asymptotic value. The explanation is that increasing the initiator concentration results in a lesser solvation of the ion-pairs at a constant promoter concentration. However at the same time there are more growing chains. The decrease in activity of the ion-pairs by lesser solvation is offset by the increase in the number of growing chains. The latter statement is verified by the fact that increasing the initiator concentration results in a decrease in molecular weight of the polymer.

In the course of this study it was found that when theinitiator concentration was varied, the rate of polymerization showed a maxima

and then decreased when the total volume of the solution was not maintained constant. By using benzene as an inert solvent and compensating for the volume of initiator added, it was possible to maintain the volume of the solution constant. When the total volume of the solution was kept constant, the asymptotic behavior was observed. This might be the reason Yuzhelevskii[30] et al. observed the maxima. It was not possible from their experimental details to ascertain if the total volume of the solution was kept constant.

4. The Effect of Initiator Concentration Upon the Molecular Weight and the Molecular Weight Distribution

The peak molecular weights and the relative areas of the peaks (if bimodal distribution was observed) obtained from the GPC chromatograms of the samples at various initiator concentrations at a constant THF concentration of 1.574 mole/liter are presented in Table VI.

An inspection of Table VI shows that as the initiator concentration is decreased, the molecular weight increases. Further the amount of the higher molecular weight fraction (which arises due to the water present in the system) increases with decreasing initiator concentration. When the initiator concentration is much higher than the water concentration, a monomodal and relatively narrow distribution polymer results, and the peak molecular weight is proportional to the number of initiator species present in the system. The number average molecular weight $\overline{M}_n$ calculated for an initiator concentration of 24.0 x 10^{-3} mole/liter is 7,200 and the peak molecular weight obtained for this polymer from GPC measurements is 12,000. This apparent discrepancy between $\overline{M}_n$ and $\overline{M}_p$ may be attributed to calibration factors in

TABLE VI

VARIATION OF MOLECULAR WEIGHT AND MOLECULAR WEIGHT DISTRIBUTION WITH INITIATOR CONCENTRATION AT A CONSTANT THF CONCENTRATION[a]

[Initiator] x 10^3	$\frac{[\text{Initiator}]}{[H_2O]}$	Peak Molecular Weight M_{p_1}	% Area	Peak Molecular Weight M_{p_2}	% Area	Weighted M_p
24.0	21.28	12,000	100	---	---	12,000
12.0	9.62	19,500	69	39,000	31	25,270
6.0	4.57	25,000	49	50,000	51	37,700
3.0	2.23	36,000	40	72,000	60	57,600
1.2	0.88	39,000	24	78,000	76	68,600
0.6	0.44	39,000	18	78,000	82	71,000

[a]In benzene at 31.7°

GPC, since comparisons are made relative to polystyrene standards and in reality are based upon hydrodynamic volumes.

The distribution obtained at high initiator concentration is monomodal because the concentration of lithium hydroxide formed by hydrolysis is small relative to the unhydrolyzed initiator. The lithium hydroxide formed initiates difunctional polymers which grow at both ends. However as the amount of difunctional polymers formed is small compared to the monofunctional polymers it is not seen in the GPC chromatogram.

When the initiator concentration is small relative to the water concentration, a large portion of the initiator is hydrolyzed to lithium hydroxide which is responsible for the formation of the high molecular weight peak (82%). It should be realized that both the monomer and water compete for reaction with the initiator with the result that although water is in excess, a small amount of the monofunctional polymers is still obtained. Whenever a bimodal distribution is obtained, calculation of $\overline{M}_n$ depends on the concentrations of initiator and water, because the latter acts as a co-initiator. The GPC chromatograms obtained at three different initiator concentrations of 24.0×10^{-3}, 6.0×10^{-3} and 0.6×10^{-3} mole/liter are reproduced in Figure 6.

In order to arrive at a relation for calculating $\overline{M}_n$ when bimodal distribution is observed, the total water content introduced into the system is required. In the data presented in Table V and VI, the water concentration was the minimum amount introduced by benzene and THF alone. The total amount of water in the system was unknown. An alternative approach for determining the total amount of water was utilizing the areas from the GPC chromatograms. As seen from Table VI, the areas

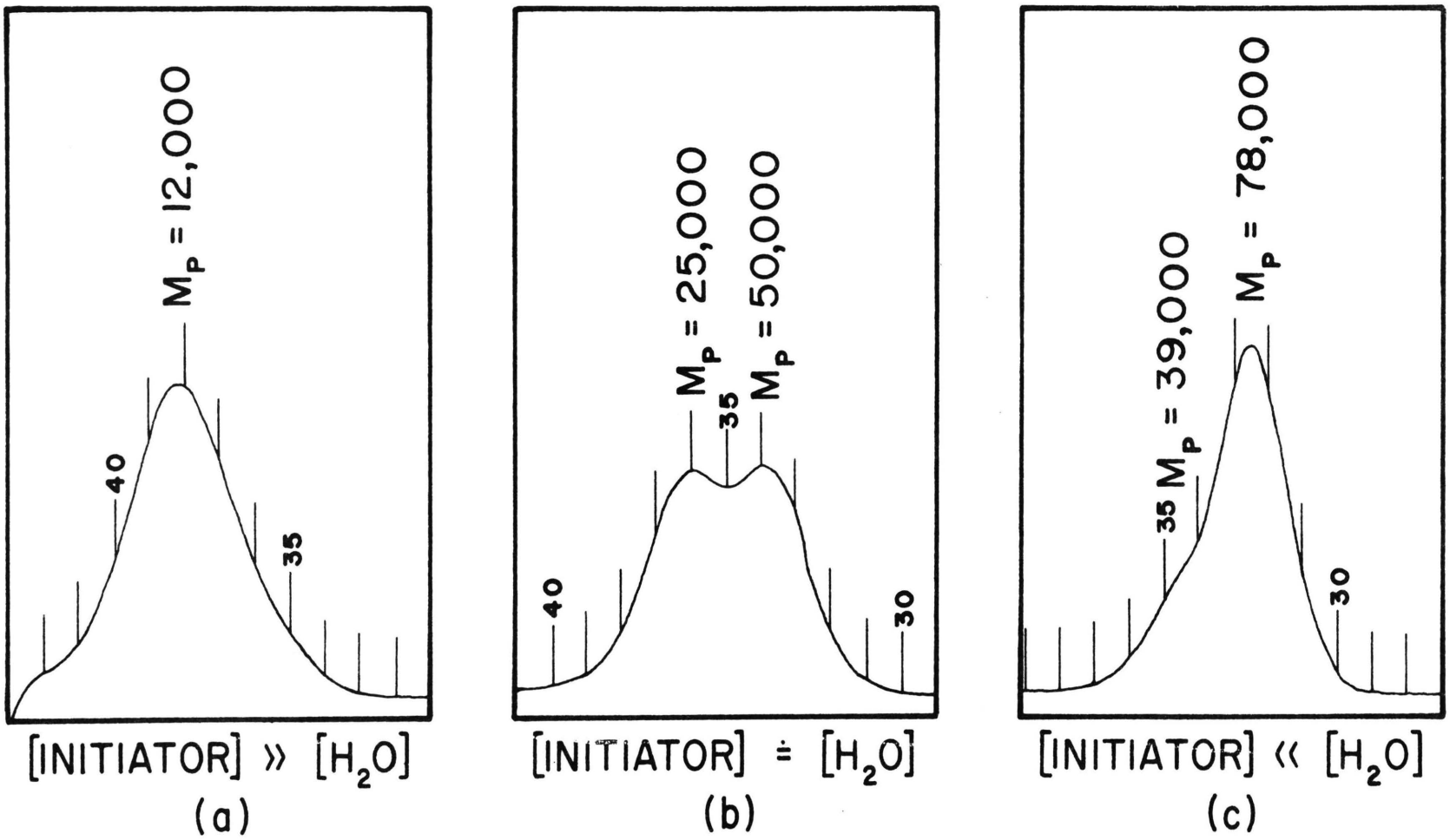


Figure 6. GPC Chromatograms of Polymer A at Initiator Concentrations of (a) 24.0 x 10^{-3} Moles/Liter, (b) 6.0 x 10^{-3} Moles/Liter and (c) 0.6 x 10^{-3} Moles/Liter

of the bimodals are approximately equal at an initiator concentration of 6.0×10^{-3} mole/liter. This shows that the concentration of lithium hydroxide produced by hydrolysis is equal to that of the monofunctional initiator and hence the total water content is 3.0×10^{-3} mole/liter.

A relationship is proposed for the calculation of $\overline{M}_n$ which takes into account the formation of monofunctional and difunctional polymers.

$$\overline{M}_n = \frac{[\text{Monomer}] \times \text{Mol. Wt. of Monomer}}{[\text{Initiator}]_1 + [H_2O]}$$

$[\text{Initiator}]_1$ = Monofunctional initiator concentration

In the above relation the concentration of monofunctional initiator is calculated from the % area of the monofunctional peak. The concentration of water responsible for the formation of difunctional polymer is included in the denominator. Using the above relationship and assuming a total water concentration of 3.0×10^{-3} mole/liter, the $\overline{M}_n$ calculated at various initiator concentrations is presented in Table VII.

TABLE VII

COMPARISON OF NUMBER AVERAGE MOLECULAR WEIGHT WITH WEIGHTED PEAK MOLECULAR WEIGHT

$[\text{Initiator}] \times 10^3$	$\overline{M}_{n\ \text{calcd}}$	Weighted M_p	Deviation Factor
24.0	7,200	12,000	1.66
12.0	15,250	25,270	1.66
6.0	28,960	37,700	1.30
3.0	40,950	57,760	1.41
1.2	52,310	68,600	1.31
0.6	55,340	71,000	1.28

The proposed relationship shows a deviation and it must be considered a rough approximation. It attempts to take into account the effect of water in determining the molecular weight. This approach was taken because of the bimodal distribution. Determination of weight average molecular weight $\overline{M}_w$ by light scattering photometry, number average molecular weight $\overline{M}_n$ by osmometry, and viscosity average molecular weight $\overline{M}_v$ by intrinsic viscosity measurements would not give an accurate picture of the molecular weight profile and the results would be misleading.

The following simplifications are made in the proposed relationship.

(i) When $[\text{initiator}] >> [H_2O]$, the area of the higher molecular weight peak is negligible and the system approaches a single distribution with the initiator concentration determining $\overline{M}_n$. Thus the relationship simply reduces to $\overline{M}_n = \frac{[\text{Monomer}]}{[\text{Initiator}]} \times$ Mol. Wt. of Monomer.

(ii) When the $[H_2O] >> [\text{initiator}]$ the area of the lower molecular weight peak is negligible and the system approaches a single distribution. Here the water concentration determines the molecular weight and the relationship reduces to

$$\overline{M}_n = \frac{[\text{Monomer}]}{[H_2O]} \times \text{Mol. Wt. of Monomer.}$$

The validity of the above for excess water is pursued in Section 6.

5. The Effect of Water Concentration Upon the Rate of Polymerization of Cyclic A

The effect of water concentration on the rate of polymerization of A was determined in two ways: (a) varying the water concentration at a low initiator concentration and (b) varying the water concentration at a high initiator concentration.

a. The effect of varying the water concentration at a low initiator concentration

An initiator concentration of 2.40×10^{-3} mole/liter was used. By varying the water content in benzene and THF a water concentration of 1.1×10^{-3} mole/liter (in the "dry" run) and 8.7×10^{-3} mole/liter (in the "wet" run) is obtained. Figure 7 shows the first order plot of the polymerization of cyclic A in the "dry" and "wet" runs. The rate constants obtained from the slopes of the plots are 1.54×10^{-2} min^{-1} for the "dry" run and 1.35×10^{-2} min^{-1} for the "wet" run which represent a rate decrease of about 13% for an eightfold increase in water concentration. Figure 7 also shows that when the water concentration is increased eightfold the induction time is increased. This is explained by the fact that when water concentration is sufficiently in excess of the initiator concentration, all the initiator is hydrolyzed to LiOH before the initiator has a chance to react with the monomer. This hydrolysis represents a finite time interval which is exhibited as a longer induction period.

It was expected that after the longer induction period, the rate of propagation would be the same as in the case with the "dry" run. However the experiment showed a decrease in rate. It should be realized that when polymerization occurs in the presence of excess water, the growing chain containing $\equiv SiOLi$ end groups not only exchanges with a chain temporarily terminated as $\equiv Si\text{-}OH$ (discussed in Section 1) but also undergoes hydrolysis as shown below.

$$\equiv SiOLi + H_2O \rightleftharpoons \equiv SiOH + LiOH$$

The lithium hydroxide formed can either initiate another chain by a

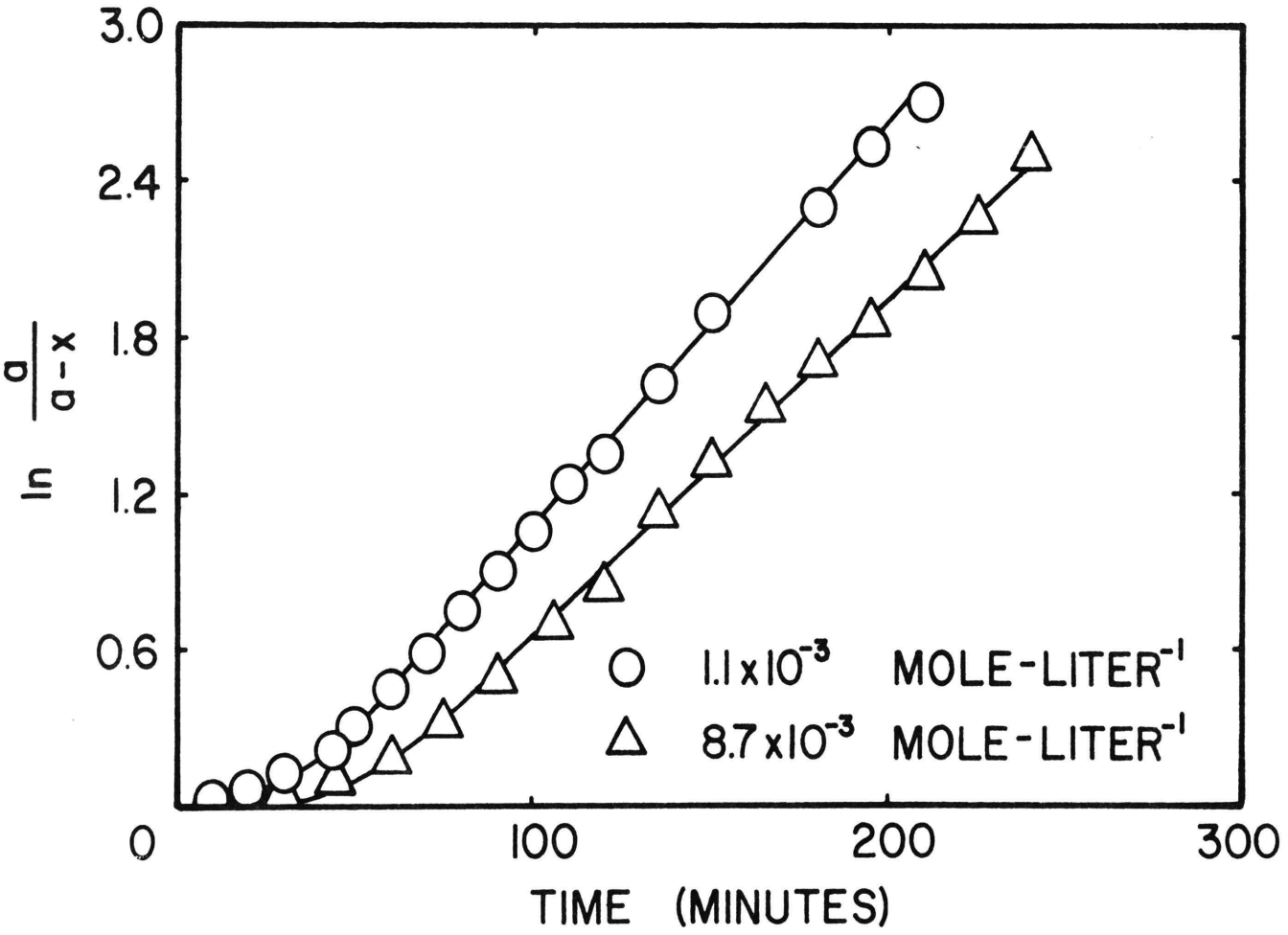


Figure 7. The Effect of Water Concentration Upon the Rate of Polymerization of Cyclic A at an Initiator Concentration of 2.40 x 10^{-3} Mole/Liter

ring-opening reaction or undergo a reversible exchange back to ≡SiOLi. The relative magnitudes of these reactions are not known but the equilibrium shown above will depend undoubtedly on the amount of water present. When the water concentration is greatly in excess of the lithium silanolate, the equilibrium will completely shift to the product. In fact this is a method for analyzing the lithium content in lithium silanolate salts by hydrolyzing them with excess water to LiOH and titrating the base. In any case the solubility of LiOH formed is very low in organic media and therefore any exchange reaction between ≡SiOH and LiOH or initiation of new chain by LiOH will lessened. Hence there is a decrease in the rate.

b. The effect of varying the water concentration at a high initiator concentration

An initiator concentration of 24.0×10^{-3} mole/liter was used. The water concentration in the "dry" run was 1.0×10^{-3} mole/liter, and by using THF with a water content of 3600 ppm, a water concentration of 25.0×10^{-3} mole/liter was obtained for the "wet" run. Figure 8 shows the first order plot of the polymerization of cyclic A in the "dry" and "wet" runs. The rate constants obtained are 0.208 min^{-1} and 0.200 min^{-1} respectively. The induction time was slightly increased but the rate constant was essentially the same. Though the water concentration in the "wet" run was approximately 25 times greater than that of the "dry" run, the initiator concentration was so high that even in the "wet" run, the initiator concentration was approximately equal to the water concentration.

The study of the effect of water on the rate of polymerization of cyclic A at low and high initiator concentrations shows the ratio of

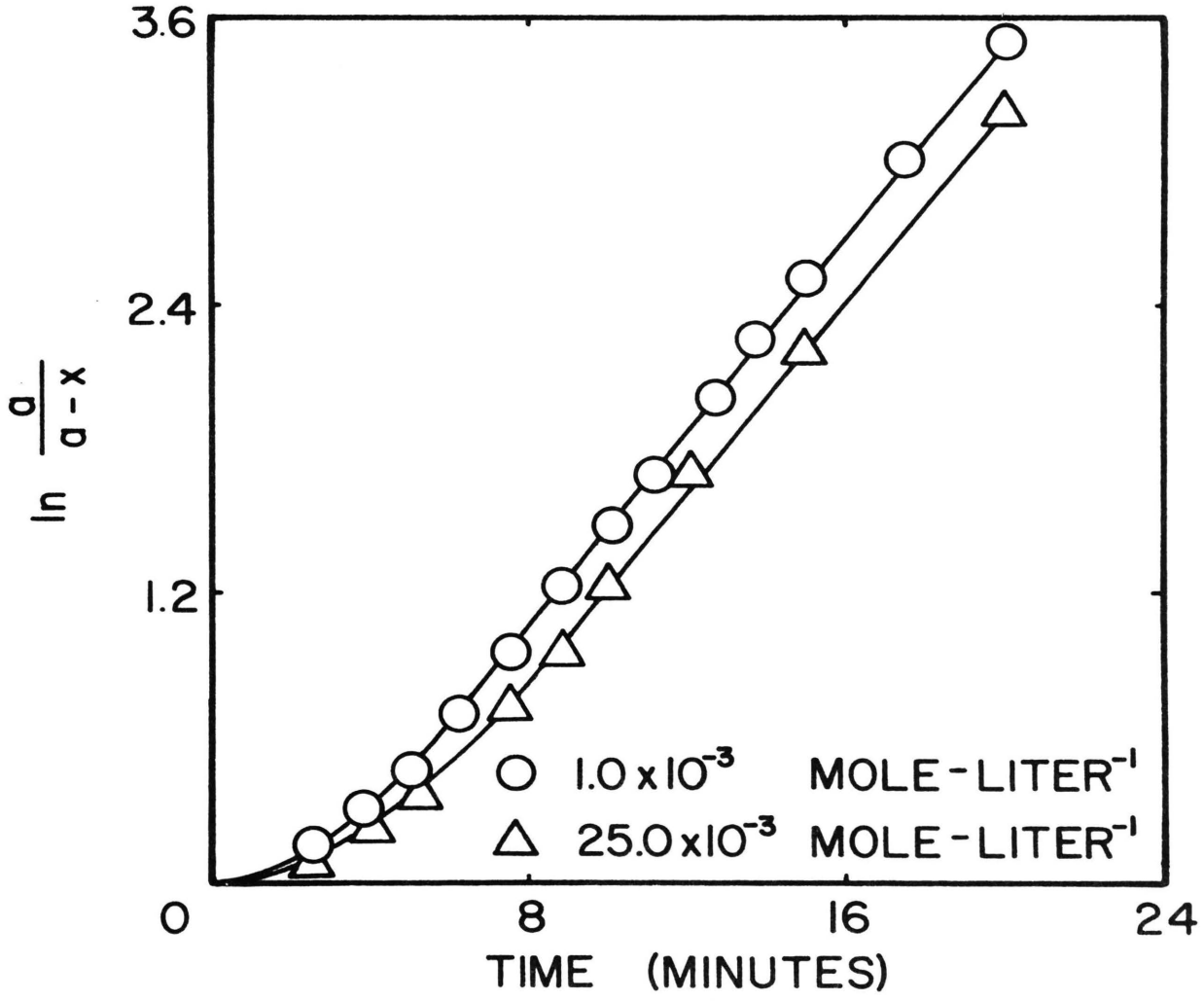


Figure 8. The Effect of Water Concentration Upon the Rate of Polymerization of Cyclic A at an Initiator Concentration of 24.0 x 10^{-3} Moles/Liter

initiator to water concentration is important in the rate measurements. At high initiator concentrations a large water content can be tolerated without any significant change in the overall rate of polymerization. At low initiator concentrations a large water content decreases the overall rate. The minimum water concentration in all measurements was about 1.0×10^{-3} mole/liter. The initiator concentration varied from 0.6×10^{-3} mole/liter at the lowest level to 24.0×10^{-3} mole/liter at the highest level. Thus the initiator concentration was either equal to or for the most part greater than the water concentration. Therefore the effect of water on the rate using benzene with 30 ppm water and THF with 45 ppm water was assumed negligible.

6. The Effect of Water Concentration Upon the Molecular Weight and the Molecular Weight Distribution in the Polymerization of Cyclic A

In the previous section the importance of the ratio of the initiator to water concentration on the rate of polymerization of A was shown. In order to determine the effect of water on the molecular weight and the molecular weight distribution, the samples obtained from the study of the effect of water on the rate of polymerization of A were characterized using GPC. The results obtained are presented in Table VIII.

The effect of excess water was to reduce the molecular weight. When the initiator concentration was 2.4×10^{-3} mole/liter and the minimum water content 1.1×10^{-3} mole/liter, a bimodal distribution was observed. The reactions responsible are discussed in Section 2. When the water concentration was about 8 times greater than that of the initiator, a monomodal distribution was observed whose peak molecular weight was less than that obtained in the "dry" run. The

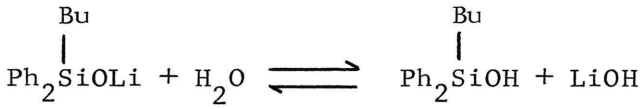
TABLE VIII

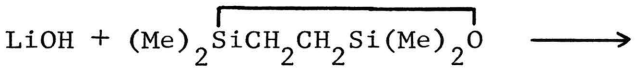
EFFECT OF WATER UPON THE MOLECULAR WEIGHT AND THE MOLECULAR WEIGHT DISTRIBUTION[a]

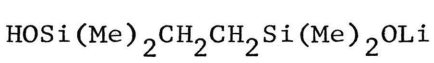
$[Initiator] \times 10^3$	Minimum $[water] \times 10^3$	Peak Molecular Weight M_{p_1}	% Area	Peak Molecular Weight M_{p_2}	% Area	Weighted M_p
2.4	1.1	30,000	32	60,000	68	50,400
2.4	8.7	30,000	100	--	--	30,000
24.0	1.0	12,000	100	--	--	12,000
24.0	25.0	7,600	100	--	--	7,600

[a] Polymerization of cyclic A in benzene at 31.7^{o}

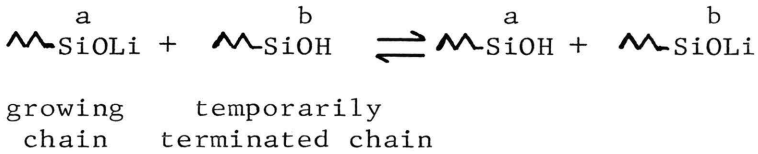
formation of a monomodal distribution is explained as follows: when the water concentration is much larger than the initiator concentration, the initiator reacts with water to form lithium hydroxide.







Due to the very fast exchange reaction shown below



the growing chain has an opportunity to grow at both ends. Further since most of the monofunctional initiator has been converted to LiOH which forms difunctional polymers, the peak due to the monofunctional initiator (which would appear at exactly half the molecular weight) is absent. It is also evident in these cases that lithium hydroxide is the initiator. The original initiator $Ph_2Si(Bu)OLi$ is converted to $Ph_2Si(Bu)OH$ and does not take part in the polymerization reaction. Thus the effect of excess water in producing a monomodal distribution is explained.

The effect of excess water in producing a monomodal distribution with a lower molecular weight is explained as follows: when the water concentration is greater than that of the initiator, the reaction of

the latter with water will produce LiOH which initiates the ring-opening polymerization.

$$LiOH + (Me)_2\overline{SiCH_2CH_2Si(Me)_2O} \longrightarrow$$

$$HOSi(Me)_2CH_2CH_2Si(Me)_2OLi$$

However water still remains after reaction with the initiator. This residual water reacts with the opened ring before any further propagation results.

$$HOSi(Me)_2CH_2CH_2Si(Me)_2OLi + H_2O \longrightarrow$$

$$HOSi(Me)_2CH_2CH_2Si(Me)_2OH + LiOH$$

The LiOH formed opens another ring to form $HOSi(Me)_2CH_2CH_2Si(Me)_2OLi$ which in turn reacts with water to form LiOH. This series of reactions continue until all the water is exhausted. Then there will be a certain number with SiOLi at one end. However because of the very fast SiOH-SiOLi exchange reaction they will have equal probability to grow producing a monodispersed polymer. However the molecular weight will depend on the water present because as shown above water is responsible for the initiation of new chains.

The validity of the relationship proposed in Section 4 can be verified from

$$\overline{M}_n = \frac{[\text{Monomer}] \times \text{Mol. wt. of Monomer}}{[H_2O]} .$$

using the minimum concentration of water present as 8.7×10^{-3} mole/liter

$$\bar{M}_n = \frac{1.073 \text{ moles/liter} \times 160.3 \text{ g/mole}}{8.7 \times 10^{-3} \text{ moles/liter}}$$

$$= 19{,}770 \text{ g/mole.}$$

The peak molecular weight obtained from the monomodal distribution is 30,000.

In the studies of the effect of water on molecular weight at the high initiator concentration, a monomodal distribution with a peak molecular weight of 7600 was observed. The minimum water content was 25.0×10^{-3} mole/liter. At this concentration, a biomodal molecular weight distribution was expected but a monomodal distribution was observed showing some additional water had entered the system.

An attempt was made to prepare a monodispersed polymer of high molecular weight by removing all traces of water. In order to achieve this, the monomers, solvents and glassware had to be dry. The glassware was baked at 200^{o} overnight. The syringes used for the addition of reactants were dried at 37^{o}. Benzene and THF were distilled from lithium aluminum hydride. A micro distillation assembly was set up inside a polythene glove bag filled with dry nitrogen. Cyclic A was distilled inside the glove bag and a middle cut taken. Appropriate quantities of the reactants were mixed in an NMR tube and allowed to polymerize. After the complete conversion of monomer to polymer, the reaction was quenched with a drop of glacial acetic acid and the polymer obtained after evaporation of the solvent. GPC characterization of the polymer showed a biomodal instead of the expected monomodal

distribution. These results dictate that all traces of water must be removed from system. This necessitates a completely closed system for all steps of the synthesis.

The study of the effect of water on the molecular weight and molecular weight distribution revealed the following:

(i) When the initiator concentration was much greater than the water concentration, a monomodal distribution was obtained whose molecular weight depended on the initiator concentration.

(ii) When the initiator concentration was approximately equal to that of water a bimodal distribution was obtained. This distribution is due to the monofunctional initiator (unhydrolyzed $Ph_2BuSiOLi$) and the other to LiOH which forms polymers capable of growing at both ends.

(iii) When the water concentration was much greater than the initiator concentration, a monomodal distribution was obtained whose molecular weight depended on the water concentration.

From the GPC chromatograms the polydispersity index $\frac{\overline{M}_w}{\overline{M}_n}$, was calculated for the extreme cases where monomodal distributions occurred. The data for the polymer obtained at an initiator concentration of 2.4×10^{-3} mole/liter and water concentration of 8.7×10^{-3} mole/liter are presented in Table IX.

The number average molecular weight $\overline{M}_n$, is defined[50] as

$$\overline{M}_n = \frac{\Sigma N_i M_i}{\Sigma N_i} = \frac{\Sigma H_i}{\Sigma (H_i/M_i)} .$$

TABLE IX

CALCULATION OF $\bar{M}_w$ / $\bar{M}_n$ FROM THE GPC CHROMATOGRAM

Count No.	H_i	$M_i \times 10^{-4}$	$(H_i/M_i) \times 10^4$	$H_i M_i \times 10^{-4}$
33.0	1.0	6.9	0.145	6.90
34.0	11.5	5.0	2.300	57.50
35.0	32.0	3.5	9.143	112.00
35.4	35.5	3.1	11.450	110.05
36.0	30.5	2.5	12.200	76.25
37.0	12.5	1.8	6.940	22.50
38.0	6.0	1.3	4.615	7.80
39.0	2.0	1.0	2.000	2.00
40.0	0.5	0.7	0.714	0.35
	$\Sigma H_i = 131.5$		$\Sigma H_i/M_i) = 49.507$	$\Sigma H_i M_i = 395.35$

The weight average molecular weight $\bar{M}_w$, is defined[50] as

$$\bar{M}_w = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i} = \frac{\Sigma H_i M_i}{\Sigma H_i} ,$$

where H_i is the height of the GPC peak from the baseline measured at a certain M_i and is equal to $N_i M_i$, the number of i the species with molecular weight M_i.

$$\therefore \bar{M}_n = \frac{131.5}{49.507 \times 10^{-4}} = \underline{26,560}$$

and $\bar{M}_w = \frac{395.35 \times 10^4}{131.5} = \underline{30,065}$.

$$\therefore \text{ The polydispersity index } \frac{\bar{M}_w}{\bar{M}_n} = \frac{30,065}{26,560} = 1.13$$

The polydispersity index of 1.13 shows that the polymer is of narrow molecular weight distribution.

7. The Effect of Substituting Phenyl Groups Upon the Rate of Polymerization of Cyclocarbosiloxanes

The rate constants obtained at 31.7° for the homopolymerization of different cyclic monomers at the same concentrations of monomer, promoter and initiator are listed in Table X. The cyclics B and D were found to have appreciable quantities of water (from the molecular weight determination). They were dried by azeotroping the water with benzene and then fractionally distilling the monomer under vacuum. This treatment was found to remove water, as the molecular weight obtained on polymerization was higher. The rate data reported for B and D in Table X were obtained after azeotropic distillation.

TABLE X

THE RATE CONSTANTS FOR THE HOMOPOLYMERIZATION OF CYCLOCARBOSILOXANES[a,b]

Cyclic Monomer	Structure	Rate Constant x 10^2 min^{-1}
A	$(Me)_2\overline{SiCH_2CH_2(Me)_2SiO}$	6.90
B	$(Me)_2\overline{SiCH_2CH_2(Me)(Ph)SiO}$	4.70
C	$(Ph)(Me)\overline{SiCH_2CH_2(Me)(Ph)SiO}$	7.30
D	$(Ph)_2\overline{SiCH_2CH_2(Me)_2SiO}$	0.50
E	$(Ph)_2\overline{SiCH_2CH_2(Me)(Ph)SiO}$	1.25
F	$(Ph)_2\overline{SiCH_2CH_2(Ph)_2SiO}$	----

[a] In benzene at 31.7°

[b] The first order plots of polymerization of cyclics B, C, D and E are given in Appendix C.

In order to explain the effect of phenyl for methyl substitution on the rate of polymerization of the cyclic monomers, the following points should be considered:

(i) Effect of phenyl substitution on the ring strain,

(ii) Electronic effect of phenyl substitution on the silicon atom in the ring,

(iii) Steric effect of phenyl substitution on the silicon atom in the ring,

(iv) Electronic effect of phenyl substitution on the silicon atom in the growing chain, and

(v) Steric effect of phenyl substitution on the silicon atom in the growing chain.

a. Effect of phenyl substitution on the ring strain

Phenyl substitution increases the strain in the ring. This is evident from Table II where the absorption frequency of the Si-O-Si bond is shifted to lower wavelengths on phenyl substitution. The effect of increasing ring strain should be to increase the ease of polymerizability of the cyclic monomers in going from A to F.

b. Electronic effect of phenyl substitution on the silicon atom in the ring

Phenyl groups are electron withdrawing by inductive effects and the effect of substituting phenyl for methyl groups is to make the silicon atom in the ring more acidic on the basis of Lewis acid-base theory. Baney and Atkari[51] titrated potentiometrically a variety of cyclosiloxanes and cyclocarbosiloxanes as very weak acids with tetra-n-butylammonium hydroxide titrant in pyridine. They determined the

half-neutralization voltages of a variety of cyclosiloxanes which included A, E and F. While there was no detectable end point for A, the half-neutralization voltages were -0.85 volts for F and -0.91 volts for E. Further the potential break at the end point became sharper with increasing acid strengths as in F or in other cyclosiloxanes containing highly electron withdrawing fluorocarbon groups. Thus the acid strength of these cyclics increases with increasing phenyl substitution, and their reactivity to a particular base increases with increasing phenyl substitution.

The effect of substituting phenyl groups on the reactivity of the ring was determined by Merker and Scott[52] by copolymerization studies on these cyclocarbosiloxanes. This study was conducted by copolymerizing two cyclic monomers either in bulk or in solution using potassium silanolate catalyst. At about 20% conversion the polymerization reaction was quenched, and the copolymer isolated by precipitation in methanol. From the weight and the refractive index of the copolymer they were able to determine the percent cyclic monomers that formed the copolymer. By using different pairs of cyclic monomers, they arrived at the following reactivity ratios which, normalized to A, are given in Table XI.

TABLE XI

RELATIVE REACTIVITIES OF CYCLOCARBOSILOXANES

Cyclic Monomer	Relative Reactivity
A	1.00
B	1.79
C	5.43
D	5.56
E	10.41
F	19.75

In these copolymerization studies Merker and Scott[52] neglected the catalyst specificity arising due to end-group variants in the growing chains since the conversion was low (20%). At first glance Tables X and XI may seem contradictory. This is explained in terms of the mechanism of copolymerization of two cyclic monomers as against their homopolymerization. Consider for example the copolymerization of A and F as against their homopolymerization. In the copolymerization reaction, the growing chains either with $\sim\sim(Me)_2SiO^{(-)}$ or $\sim\sim(Ph)_2SiO^{(-)}$ ends despite their large difference in reactivity, will preferentially attack F which is more acidic. Thus in the copolymerization studies in which the reaction is quenched at very low conversion, a larger amount of polymer is derived from F than from A. However in the homopolymerization of A, the growing chain end always has the structure $\sim\sim(Me)_2SiO^{(-)}$ whose reactivity determines the rate of homopolymerization. In the case of F growing chain always has the structure $\sim\sim(Ph_2SiO^{(-)}$ whose reactivity determines the rate of homopolymerization. Therefore there is no relationship between the relative reactivities obtained from copolymerization, and the rate constant obtained from homopolymerization.

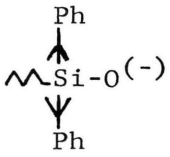
c. Steric effect of phenyl substitution on the silicon atom in the ring

Substitution of phenyl groups for methyl groups in the ring should offer some steric hindrance to the nucleophilic attack at the silicon atom in the ring. However there is no quantitative way to determine the magnitude of the steric effect. Increasing the number of phenyl groups at the silicon atom in the ring should increase the

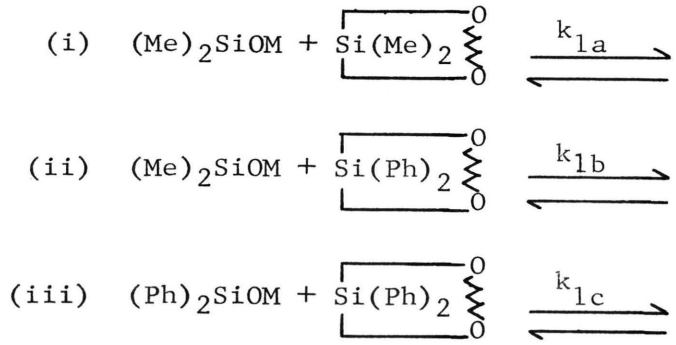
steric hindrance, and cyclics with a large number of phenyl groups should exhibit a decrease in their reactivity to bases on the basis of steric requirements alone.

d. Electronic effect of phenyl substitution on the silicon atom in the growing chain

Substitution of phenyl for methyl groups in the growing chain makes the silanolate anion a weaker nucleophile because of the inductive effect.



Laita and Jelinek[53] studied the copolymerization of octamethylcyclotetrasiloxane with octaphenylcyclotetrasiloxane under the catalytic action of KOH. They determined the composition of the copolymer in the very early stages of the reaction (10% conversion), and found that octaphenylcyclotetrasiloxane polymerized prior to that of octamethylcyclotetrasiloxane. The domination of copolymerization by octaphenylcyclotetrasiloxane was explained on the basis of the reactivity of the silanolate anions, and is illustrated by the following scheme of active end variants:



(iv) $(Ph)_2SiOM + \overset{O}{\underset{O}{\ulcorner\!\!\llcorner Si(Me)_2 \sim}}$ $\xrightarrow{k_{1d}}$ $\xleftarrow{}$

Laita and Jelinek[53] rationalized, on the basis of electronic considerations, that the activity of the diphenylsilanolate growing end is much less than the activity of the dimethylsilanolate growing end because of the greater acidity of the diphenylsilanolate. Thus $k_{1b} >> k_{1c}$ and $k_{1a} >> k_{1d}$, and these relationships remain in force in spite of the different reactivities of the cyclicsiloxanes. The result is that, as long as diphenylsiloxane cyclic is available, the ionic concentration will be rich in diphenylsilanolate ions which have low reactivity toward dimethylcyclosiloxane ($k_{1c} >> k_{1d}$). The result of this copolymerization study is that on the same rationale as above, the reactivity of the growing silanolate end with different substituents on the silicon atom is in the order: $(Me)_2SiO^{(-)} > (Ph)(Me)SiO^{(-)} > (Ph)_2SiO^{(-)}$.

e. Steric effect of phenyl substitution on the silicon atom in the growing chain

Substitution of phenyl groups for methyl groups on the silicon atom in the growing chain decreases the activity of the silanolate anion due to increased steric hindrance. Due to steric requirements, the order of reactivity of the silanolate anion is postulated as $(Me)_2SiO^{(-)} > (Ph)(Me)SiO^{(-)} > (Ph)_2SiO^{(-)}$.

It is seen that the electronic effect is opposite in the growing chain from that of the ring, while the steric effect is prevalent both in the ring as well as in the growing chain. As would be expected, and also verified by molecular models of the ring and the growing chain, steric hindrance is greatest whenever the silanolate anion with the

silicon atom having two phenyl substituents $-(Ph)_2SiO^{(-)}$ attacks the silicon atom in the ring having two phenyl groups.

8. Reaction Rate Studies on the Polymerization of Cyclics B, C, D, E and F

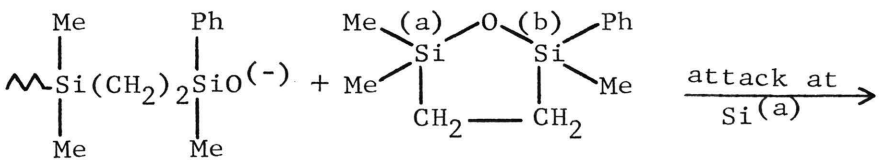
The rate constants listed in Table X for the polymerization of cyclics B, C, D and E are discussed using the information from the steric and electronic effects of phenyl substitution.

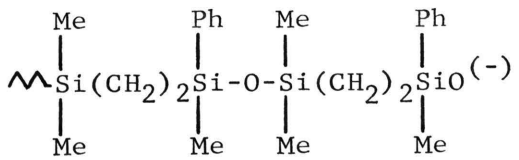
a. Polymerization of cyclic B

The NMR spectrum (CCl_4) of the polymer obtained from B showed multiplets centered at 7.32 δ ($Si-C_6H_5$) and 0.6 δ ($-CH_2CH_2-$), a singlet at 0.35 δ ($Si-CH_3$) and a doublet at 0.10 δ ($CH_3-Si-CH_3$). The doublet (Figure 9) attributed to $=Si(CH_3)_2$ protons in the polymer was also verified by obtaining the spectrum of the polymer utilizing a Varian HA-100, 100 MHz NMR spectrometer. The rate of polymerization of B was studied by following the appearance of the $=Si(CH_3)_2$ doublet in the polymer and the disappearance of the $=Si(CH_3)_2$ singlet in the monomer. The doublet attributed to $=Si(CH_3)_2$ protons in the polymer was seen even in the early stages of polymerization.

The doublet attributed to $=Si(CH_3)_2$ protons in the polymer can arise because of the following different possible ring-opening propagation reactions:

(i)





(I)

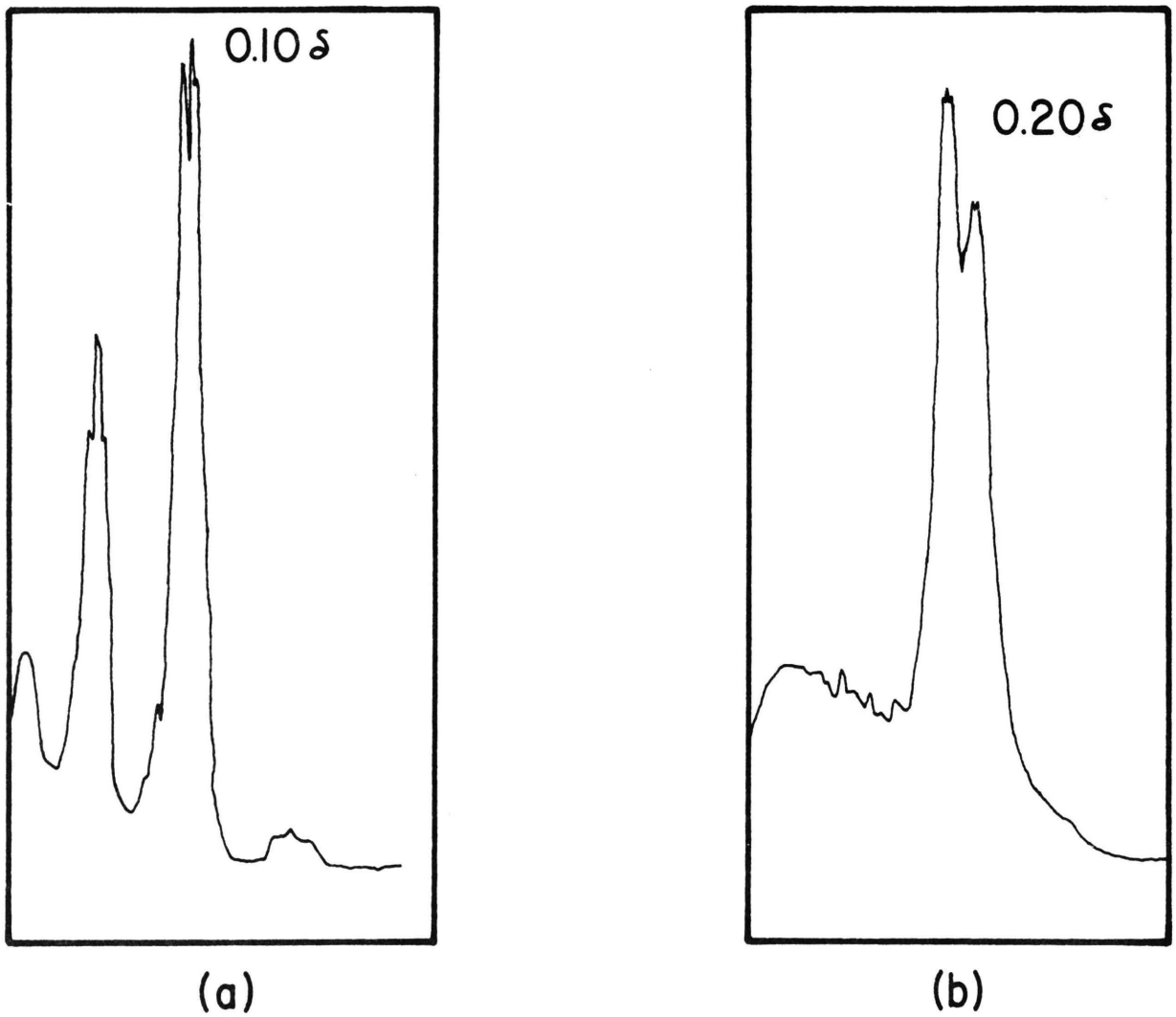
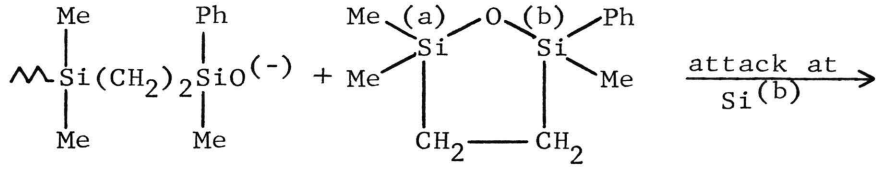
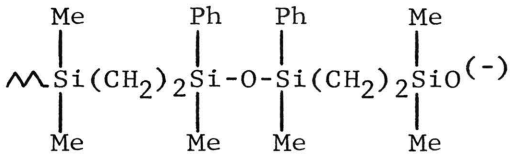
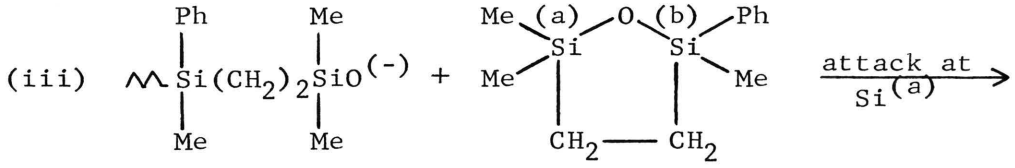


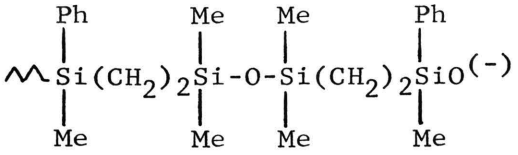
Figure 9. A Portion of NMR Spectra of (a) Polymer B and (b) Polymer D

(ii) 

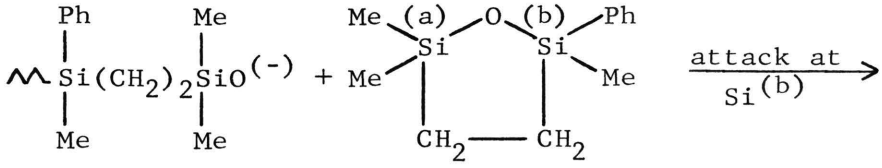


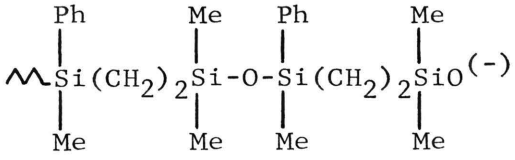
(II)

(iii) 



(III)

(iv) 



(IV)

The environment about $=Si(CH_3)_2$ protons is similar to that in the growing chains (I) and (IV), and in (II) and (III). In (I) and (IV) the $=Si(CH_3)_2$ protons are immediately surrounded by -OSi(Ph)(Me) groups whereas in (II) and (III) the $=Si(CH_3)_2$ protons are separated from -OSi(Ph)(Me) by $-CH_2CH_2-$ groups. The inductive effect of the phenyl group is to shift the position of the $=Si(CH_3)_2$ proton peak downfield. This effect of the phenyl group on the $=Si(CH_3)_2$ protons is operative more in (I) and (IV) than in (II) and (III) because the effect decreases with distance. In (II) and (III) the $=Si(CH_3)_2$ protons are separated from the silicon atom having the phenyl group by two methylene groups while in (I) and (IV) the $=Si(CH_3)_2$ protons are separated from the silicon atom having the phenyl group only by an oxygen atom. Therefore the inductive effect of the phenyl group on $=Si(CH_3)_2$ protons is felt more in (I) and (IV). This lowers the electron density around the vicinity of the proton and causes deshielding. Thus the $=Si(CH_3)_2$ protons in (I) and (IV) are shifted downfield compared to that in (II) and (III) causing the formation of the doublet.

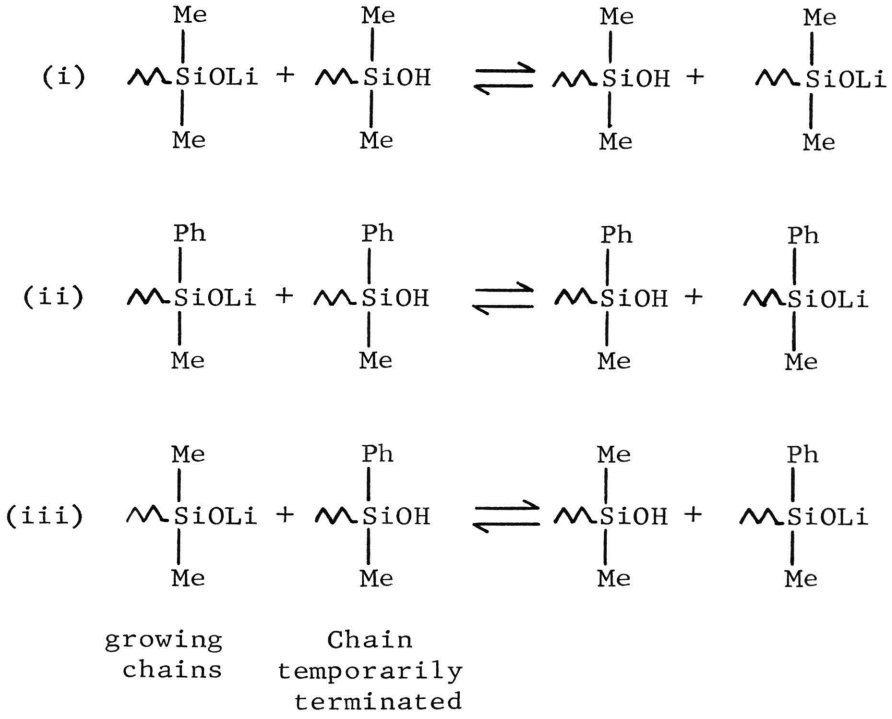
The formation of the doublet was also expected for the methyl protons =Si(Ph)(Me) because of the unequal environment around $\equiv Si(CH_3)$ groups in the growing chains. The NMR spectrum of this group of protons did show a small separation of 2 ppm sweep width.

If the ring-opening reaction always takes place by nucleophilic attack on one particular silicon atom in B, then all the growing ends, have the same structure, and the $=Si(CH_3)_2$ peak shows up as a distinct singlet. Therefore the important information obtained from the NMR spectrum of the polymer is that the ring-opening on B takes place by a nucleophilic attack on both silicon atoms.

From the proposed reaction scheme of formation of the $=Si(CH_3)_2$ doublet, it is seen that there are four propagating steps with different rate constants. The rate data obtained from NMR measurements represent the combination of all four reactions. However the first order plot obtained from the conversion data for the polymerization of B is linear without any breaks indicating all four reactions are proceeding simultaneously. The lowering of the rate constant from 0.69 to 0.47 min^{-1} in going from A to B indicates that the activity of the silanolate anion $\sim\!\!\sim(Ph)(Me)SiO^{(-)}$ is less than the activity of the silanolate anion $\sim\!\!\sim(Me)_2SiO^{(-)}$ due to both the steric and electronic effects. This reduction in reactivity of the growing chain is more than the increase in the reactivity of the ring upon introducing a phenyl group.

Initial polymerization studies on B were conducted on samples which had appreciable quantities of water, and the rate constant obtained was 0.03 min^{-1}. GPC characterization of the polymer obtained from this polymerization run showed a monomodal distribution with a peak molecular weight of 13,000. The low molecular weight indicated a large amount of water with respect to the initiator in the system. Since the benzene and THF had a water content of approximately 30 and 45 ppm, it was conceivable that B contained appreciable quantities of water. Azeotropic distillation with benzene followed by fractionation under vacuum through a 6 inch Vigreux column yielded B which yielded a polymer with bimodal distribution and peak molecular weights of 22,500 (31%) and 45,000 (69%). The rate constant obtained with this

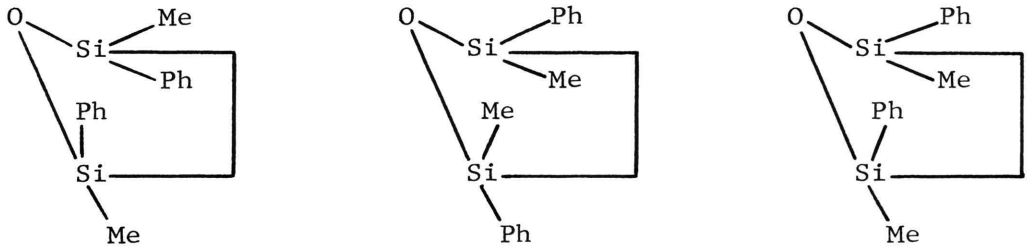
sample was 0.047 min^{-1}. The decrease in rate as the result of water was larger than that of cyclic A, and can be explained by means of the following silanol-silanolate exchange reactions.



The silanol-silanolate exchange reactions (i) and (ii) do not alter the end groups in the growing chain. However the cross silanol-silanolate exchange reaction represented in (iii) leads to the formation of the growing chain with the ~~(Ph)(Me)SiOLi end group whose reactivity is less than that of ~~$(Me)_2SiO^{(-)}$. The equilibrium in reaction (iii) probably lies more towards ~~(Ph)(Me)SiOLi because of the stability introduced through phenyl substitution. In the presence of large amounts of water there are large number of chains that are OH terminated, increasing the probability of the silanol-silanolate exchange reactions (i), (ii) and (iii). The exchange reaction (iii) leads to a decrease in the rate of polymerization.

b. Polymerization of cyclic C

Cyclic C is symmetric, and therefore nucleophilic attack on either silicon atom in the ring leads to the formation of the silanolate anion with the same substituents on the silicon atom. However C was approximately a 55:45 cis-trans mixture, and can exist in 3 different forms as shown in the following sawhorse representations.



trans (dl pair) cis (meso)

The rate data reported for C were obtained on the cis-trans mixture. It has been shown[54] that for triphenyltrimethylcyclotrisiloxane in the cis and trans forms, the reactivity of the cis-cyclic is twice that of the trans-cyclic. The increased activity of the cis over trans-cyclic results from the increased steric strain due to the crowding of the phenyl groups thereby weakening the Si-O-Si bond. The same considerations apply in C.

The rate data obtained for the polymerization of C indicate that it reacts as fast as A. This was unexpected because the silanolate anion in the growing chain from C always has the structure $\sim\!\!\sim(Ph)(Me)SiO^{(-)}$. This anion's reactivity is less than that of $\sim\!\!\sim(Me)_2SiO^{(-)}$, and accordingly the rate of polymerization should be lower than that of A.

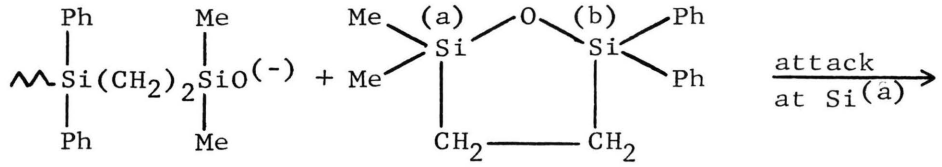
However because of steric crowding in cis-cyclic C, the Si-O-Si bond is weakened increasing the ease of nucleophilic attack. The

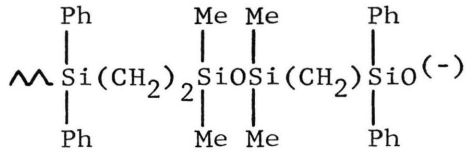
increase in the ring strain of C compared to A is shown somewhat in the lowering of the Si-O-Si stretching frequency from 924 to 915 cm^{-1} (Table II).

c. Polymerization of cyclic D

The NMR spectrum (CCl_4) of the polymer obtained from D showed multiplets centered at 7.40 δ ($Si-C_6H_5$) and 0.75 δ ($-CH_2CH_2-$) and a doublet at 0.20 δ ($CH_3-Si-CH_3$). The doublet (Figure 9) attributed to $=Si(CH_3)_2$ protons in the polymer arises because of the following different possible ring-opening propagation reactions.

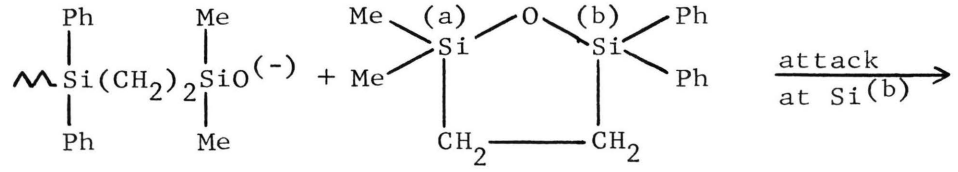
(i)

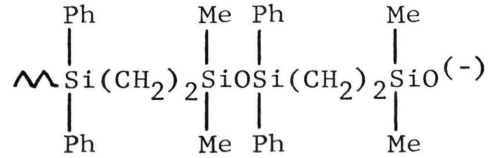




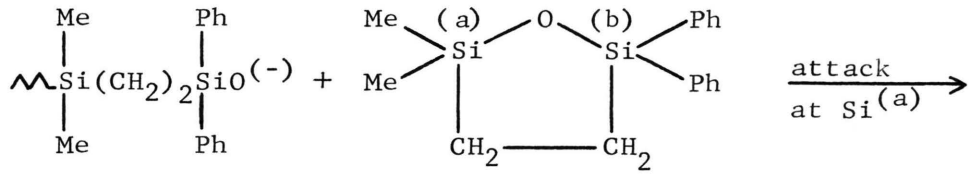
(I)

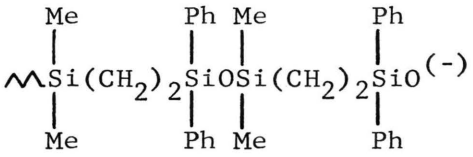
(ii)



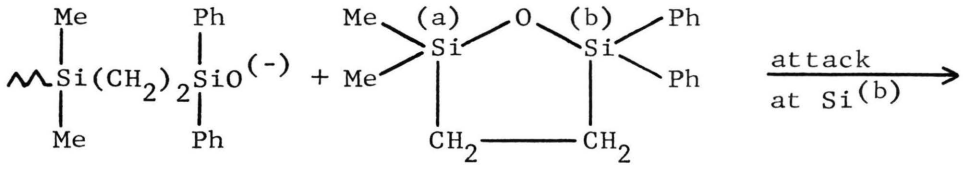


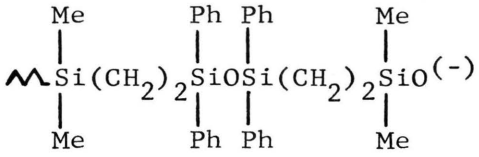
(II)

(iii) 



(III)

(iv) 



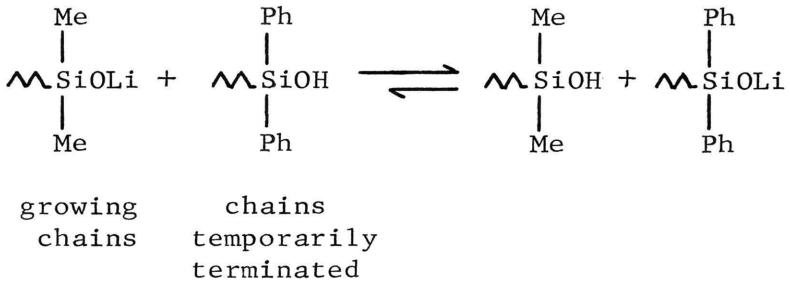
(IV)

The environment about $=Si(CH_3)_2$ protons is similar in the growing chains (I) and (IV) and in (II and (III). In (I) and (IV) the $=Si(CH_3)_2$ protons are immediately surrounded by $-OSi(Ph)_2$ groups whereas in (II) and (III), the $=Si(CH_3)_2$ protons are separated from $-OSi(Ph)_2$ groups by $-CH_2CH_2-$ groups. As explained for B, the inductive effect of the phenyl groups results in the formation of a doublet for the $=Si(CH_3)_2$ protons. Figure 9 shows that the $=Si(CH_3)_2$ doublet is not symmetrical, indicating some preference for attack at either of the silicon atoms. A closer examination of the propagating reaction scheme for D indicates

that the least reactive and the least preferred would be the nucleophilic attack of the silanolate anion $(Ph)_2SiO^{(-)}$ on the silicon atom in the ring having two phenyl groups (reaction iv). If this is so, then the area of unsymmetrical doublet should be greater towards the downfield region than the upfield region in the NMR spectrum. This is seen in Figure 9 indicating less preference for attack by the silanolate anion $(Ph)_2SiO^{(-)}$ at the silicon atom in the ring having two phenyl groups.

The decrease in rate of polymerization of D from that of others results because of the large decrease in reactivity of the silanolate anion $(Ph)_2SiO^{(-)}$ towards the ring due to electronic and steric effects. The formation of the doublet in the NMR spectrum of the polymer shows that $(Ph)_2SiO^{(-)}$ is the active end of the growing chain at least part of the time, and hence the decrease in rate of polymerization of D.

The rate of polymerization of D and the molecular weight of the polymer decreased in the presence of excess water. The first order plot for the polymerization of D before azeotropic distillation showed two different slopes of 8 and 5×10^{-4} min^{-1}, and the GPC characterization showed a single distribution with a peak molecular weight of 11,000. After azeotropic distillation the first order plot showed a slope of 5×10^{-3} min^{-1} and the GPC chromatogram showed a bimodal distribution with peak molecular weights of 16,000 (55%) and 32,000 (45%). The decrease in rate as the result of water is explained by means of the cross silanol-silanolate exchange reaction.



The equilibrium shown above undoubtedly lies towards the right because of the stability introduced by phenyl groups. The increase in water content increases the probability of this exchange reaction, and the silanolate anion $\sim(Ph)_2SiO^{(-)}$ is much less reactive than $\sim(Me)_2SiO^{(-)}$ and therefore the rate of polymerization is decreased.

d. Polymerization of cyclic E

The NMR spectrum (CCl_4) of the polymer obtained from E showed multiplets centered at 7.50 δ (Si-C_6H_5) and 1.00 δ (-CH_2CH_2-) and a singlet at 0.20 δ (Si-CH_3). If the ring-opening propagation reaction was proceeding by a nucleophilic attack on both the silicon atoms in the ring, then the $\equiv Si(CH_3)$ protons appear as a doublet because of the environment around the protons. However the NMR spectrum of the polymer showed the $\equiv Si(CH_3)$ protons only as a singlet even on an expanded scale of 2 ppm sweep width in a Varian EM 360 NMR spectrometer. This was also verified in a Varian HA-100, 100 MHz NMR spectrometer. The appearance of $\equiv Si(CH_3)$ protons as a singlet indicates that the ring-opening polymerization of E takes place by a nucleophilic attack on a particular silicon atom in the ring leading to growing chains with the growing end always having the same structure. The ring-opening reaction can take place on either the silicon atom in the ring having

two phenyl groups or on the silicon atom in the ring having a phenyl and a methyl group. The latter reaction will lead to chains having a silanolate anion with the structure $\sim(Ph)_2SiO^{(-)}$ as the growing ends. Gilman and his coworkers[55] found in their studies on the reaction of organolithium compounds with linear siloxane compounds that nucleophilic attack occurs preferentially at the silicon atom having the lower electron density and hence providing a better site for reaction. On this basis it would be expected that the ring is opening preferentially by the attack at the silicon atom having two phenyl groups. This would lead always to the formation of growing chains with the silanolate anion $\sim(Ph)(Me)SiO^{(-)}$ as the growing end. Thus the rate of polymerization of E is dependent on the attack of the $\sim(Ph)(Me)SiO^{(-)}$ anion at the silicon atom in the ring having two phenyl group. Due to the lower reactivity of the $\sim(Ph)(Me)SiO^{(-)}$ anion and steric hindrance at the $(Ph)_2Si$ portion of the ring, the rate of polymerization of E is less than that of A, B and C.

e. Polymerization of cyclic F

The polymer formed from F precipitated out of solution and therefore no rate data were obtained. Piccoli et al.[7] reported that E polymerized in bulk to a tough high polymer in 20 minutes at 120°-130° in the presence of a trace amount of potassium dimethylsilanolate catalyst. At 100° and in the presence of the same catalyst F in diphenylether solution polymerized and precipitated out of solution in 18.75 hours. Though this study was highly qualitative, it can be said that F polymerizes slower than E. This can be explained because in the polymerization of F the growing end always has the structure

$\sim\!\!\sim(Ph)_2SiO^{(-)}$ which is the least reactive in the ring-opening propagation reaction, of the three end group variants discussed before.

At this juncture some of the literature reported on the polymerization of phenyl-substituted cyclosiloxanes is discussed. Andrianov and his coworkers[56] studied the polymerization of heptamethylphenylcyclotetrasiloxane, hexamethyldiphenylcyclotetrasiloxane, octamethylcyclotetrasiloxane and tetramethyltetraphenylcyclotetrasiloxane at 150° in the presence of 0.5% KOH. They found that while heptamethylphenylcyclotetrasiloxane and hexamethyldiphenylcyclotetrasiloxane polymerized faster than octamethylcyclotetrasiloxane, tetramethyltetraphenylcyclotetrasiloxane polymerized about 50 times slower. The increase in rate of polymerization of heptamethylphenylcyclotetrasiloxane was explained as due to the increased reactivity of the ring on phenyl substitution. Their mechanism assumed the ring-opening reaction as always taking place at the silicon atom in the ring having the phenyl group.

$$(Me)_2\overbrace{SiO(Me)_2SiO(Me)_2SiO(Ph)(Me)SiO} + \sim\!\!\sim(Me)_2SiOK \longrightarrow$$

$$(Me)_2SiO(Ph)(Me)SiO(Me)_2SiO(Me)_2SiO(Me)_2SiOK$$

Thus in their scheme the ring-opening reaction always led to a growing chain end group whose structure was the same. However in this study it has been shown that the ring-opening reaction may or may not take place exclusively at one silicon atom. The decrease in the rate of polymerization of tetramethyltetraphenylcyclotetrasiloxane from octamethylcyclotetrasiloxane was attributed[56] to the steric hindrance

caused by the phenyl groups. However Chiang and his coworkers[57] by means of copolymerization studies found the reactivity of the cyclic tetramer, tetramethyltetraphenylcyclotetrasiloxane to be greater than that of octamethylcyclotetrasiloxane. This shows that the activity of the growing chain is important in determining the rates of homopolymerization, and the reactivity of the ring obtained from copolymerization studies is not useful in predicting its homopolymerizability.

The molecular weight and the molecular weight distribution for the polymers B through E obtained at the same initiator and promoter concentrations are presented in Table XII.

TABLE XII

MOLECULAR WEIGHT AND MOLECULAR WEIGHT DISTRIBUTION OF POLYMERS B THROUGH E[a]

Polymer	Peak Molecular Weight M_{p_1}	% Area	Peak Molecular Weight M_{p_2}	% Area
Polymer B	22,500	31	45,000	69
Polymer C	30,000	32	60,000	68
Polymer D	16,000	55	32,000	45
Polymer E	25,000	41	50,000	59

[a] In benzene at 31.7°

Table XII shows a bimodal distribution is obtained in all cases and the area of the two peaks shows that the total water content is comparable. However no comparison of $\bar{M}_n$ and peak molecular weight was made because of the different hydrodynamic volume of each polymer.

The homopolymerization of the cyclocarbosiloxanes investigated under the same conditions of temperature, monomer, initiator and promoter concentration suggests that it is the reactivity of the growing end groups due to the combination of the steric and polar effects that largely determines the polymerization rate of these cyclocarbosiloxanes. The relative reactivity of the cyclocarbosiloxanes obtained from copolymerization studies is not useful in predicting the individual rates of homopolymerization because of different end groups in the growing chain.

9. The Effect of Temperature Upon the Rate of Polymerization of Cyclic Monomers

The effect of temperature upon the rate of polymerization of cyclics A, B, C and E was studied. Rate constants were obtained at 20^{o}, 31.7^{o} and 40^{o}. While the rate measurements at 31.7^{o} were obtained on an EM 360 NMR spectrometer, those at 20^{o} and 40^{o} could not be obtained on the above instrument because it was not fitted with a variable temperature probe. Efforts to obtain these data on a Varian A-56/60 NMR spectrometer were unsuccessful due to the malfunctioning of the instrument. Therefore polymerization studies at 20^{o} and 40^{o} were conducted in NMR tubes in a constant temperature bath.

The variation of rate with temperature is shown in Figure 10. The apparent activation energies obtained from the slope of the lines are tabulated along with the rate constants in Table XIII.

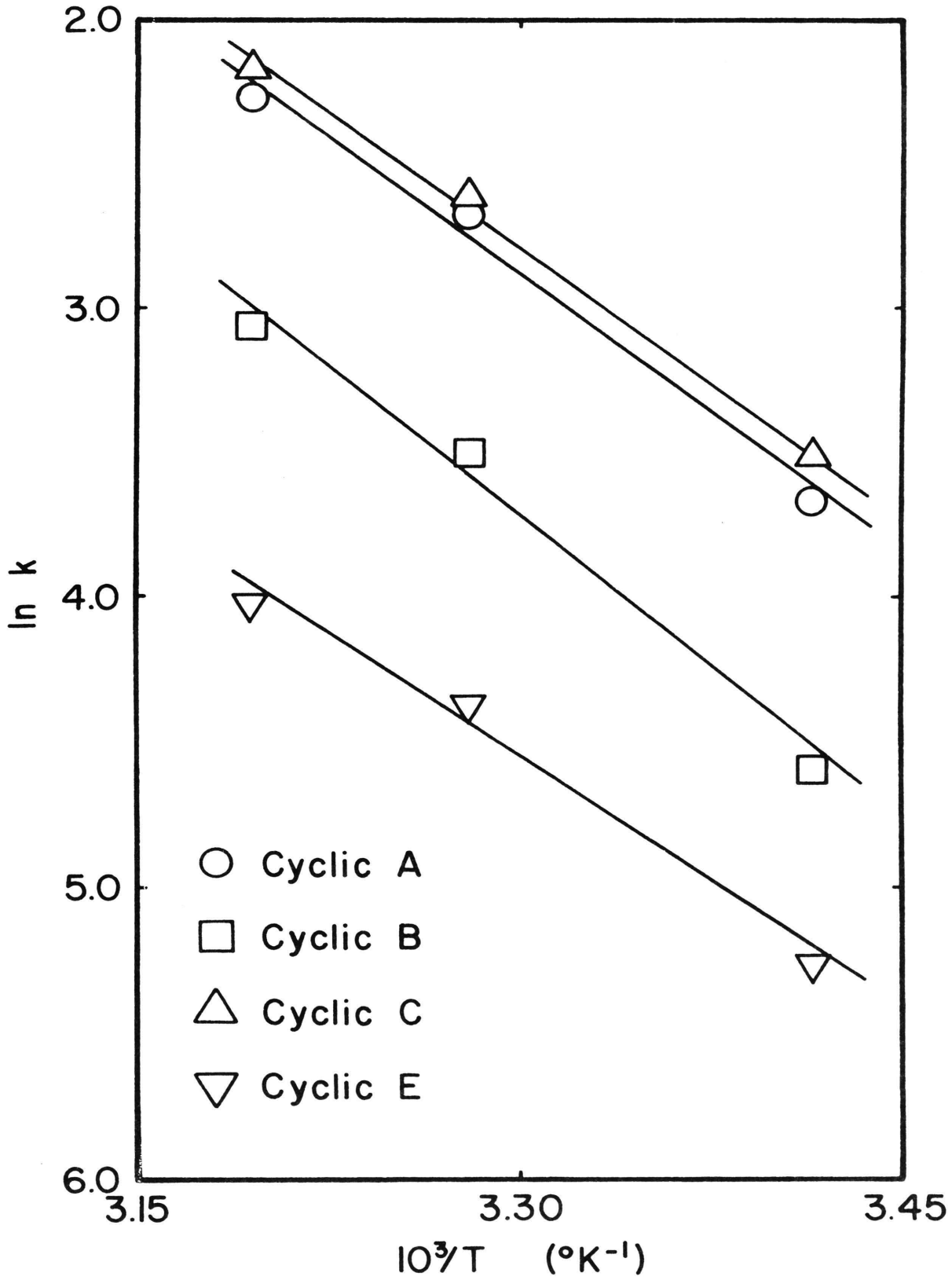


Figure 10. Dependence of Rate Constant on Temperature

TABLE XIII

TEMPERATURE DEPENDENCE OF THE RATE OF POLYMERIZATION OF CYCLICS A, B, C AND E

Cyclic Monomer	Rate constant x 10^2 min^{-1} 20^o	31.7^o	40^o	$\triangle E$ kcal/mole Apparent activation energy
A	2.50	6.90	10.30	12.7
B	1.00	3.00	4.70	13.6
C	3.00	7.30	11.50	12.3
E	0.50	1.25	1.76	11.2

Andrianov et al.[58] determined the activation energy for the anionic polymerization of the 6-membered cyclic 2,2,6,6-tetramethyl-1-oxa-2,6-disilacyclohexane as 21 kcal/mole. Sommer et al.[16] determined that the Si-O-Si absorption frequency of the ester derivative of the above 6-membered cyclic was at 1000 cm^{-1}. Sommer and Ansul[10] also determined that the Si-O-Si absorption frequency of the 7-membered ring 2,2,7,7-tetramethyl-1-oxa-2,7-disilacycloheptane was at 1018 cm^{-1}. From the above findings it can be said that in going from 6 to 7-membered cyclics, the strain in the ring does not change appreciably. It is also possible that these 6 and 7-membered cyclics are entirely strain free. However in going from the 6 to 5-membered cyclic the Si-O-Si stretching frequency is shifted from 1000 to 924 cm^{-1} indicating a high order of ring strain in the 5-membered cyclic. Piccoli et al.[7] estimated the strain energy for the cyclic series A to F to be 8-12 kcal/mole. Thus the apparent activation energy obtained in this study agrees with the value reported in the literature for the anionic

polymerization of 6-membered cyclic, assuming that the polymerization mechanism is unaltered. Studies by Morton and Bostick[27] on the anionic polymerization of octamethylcyclotetrasiloxane in the presence of THF and potassium silanolate initiator have shown that the activation energies in the promoted and the unpromoted polymerization remained the same. This indicates that the mechanism of propagation remained the same in both cases (i.e. stepwise addition).

Juliano et al.[49] have shown that the active species involved in the THF promoted oligomerization of hexamethylcyclotrisiloxane using lithium n-butyldimethylsilanolate initiator remained unchanged in the temperature region 25-60°. They obtained the NMR spectra of 33% THF solvated lithium n-butyldimethylsilanolate showing signals due to contact ion-pairs and solvated ion-pairs. They measured the area of the two signals by planimetry while varying the temperature and found that though the signals were broadened, their relative areas remained unchanged between 25-60°. This shows that the active species concentration did not change with temperature. Therefore in the present study, where the temperature was varied between 20-40°, the variation of rate with temperature was indeed due to the thermal effect and not due to changes in active species concentration.

In order to determine the effect of temperature on molecular weights, samples obtained from the polymerization of A at 20°, 31.7° and 40° were characterized by GPC. These chromatograms showed a monomodal distribution with a peak molecular weight of 26,000 for the 20° run and 25,000 for the 40° run. However the molecular weight distribution obtained on the 31.7° run showed a bimodal distribution with

peak molecular weights at 36,000 and 72,000 and a weighted peak molecular weight of 53,200. The lowering of the molecular weight in the 20 and 40° runs is possibly due to water picked up from the constant temperature bath. This will also explain why in the Arrhenius plot the data points obtained at 20 and 40° were always slightly lower, possibly indicating the presence of excess water relative to the initiator. For this reason the activation energy of polymerization should be regarded only as apparent, and the range given as 10-14 kcal/mole for the series in going from F to A.

V. CONCLUSIONS

As a result of this study the following conclusions were made:

1. The rate of polymerization of the 5-membered cyclocarbosiloxanes was measured utilizing an NMR spectrometer.

2. At a constant monomer and initiator concentration the rate of polymerization at 31.7^{o} increased and the induction time decreased when the concentration of THF was increased.

3. At a constant monomer and THF concentration the rate of polymerization at 31.7^{o} was proportional to the square root of the initiator concentration in the region $0.6 - 3.0 \times 10^{-3}$ mole/liter; the rate of polymerization remained constant beyond the initiator concentration of 3.0×10^{-3} mole/liter.

4. The rate of polymerization of cyclic A did not change significantly when the concentration of water was comparable to that of the initiator concentration; excess water concentration (in relation to the initiator concentration) decreased the rate of polymerization.

5. GPC analyses showed that both monomodal and bimodal distribution polymers could be obtained depending on the initiator and water concentration. When the initiator concentration was much greater than the water concentration or vice versa, a single distribution was obtained and the polymer was essentially monodispersed. A bimodal distribution was observed when the initiator concentration was approximately equal to that of the water concentration.

6. The weighted peak molecular weight was found to depend on the initiator and water concentration.

7. Monodispersed polymers with high molecular weight (about 10^5) were not obtained due to the water present in the system.

8. The rate of polymerization of cyclics A through F depended on the reactivity of the growing chain ends.

9. The apparent activation energy of polymerization was in the range 10 - 14 kcal/mole.

10. For the synthesis of truly ordered block copolymers by the sequence addition of cyclic monomers, cyclics B and D will probably not be useful.

11. For the synthesis of monodispersed polymers with very high molecular weights it is imperative that all traces of water be eliminated.

VI. ADDITIONAL WORK AND APPLICATIONS

The results of this investigation indicate that additional work is necessary for a more complete understanding of the polymerization of cyclocarbosiloxanes and their properties. The following areas are suggested for investigation:

1. The synthesis of high molecular weight polymers from the cyclocarbosiloxanes with single distribution is needed. This may be achieved either by using a monofunctional initiator in a completely dry system or by using a difunctional initiator. In the latter case a single distribution will be obtained regardless of the amount of water, which will however determine the molecular weight.

2. Separation of cis and trans isomers of cyclic C and a study of their polymerization behavior is needed.

3. A study of the crosslinking (vulcanizing) behavior of these polysiloxanes is needed. For room temperature vulcanization it is essential to have polysiloxanes that are terminated by hydroxyl groups on both ends of the chains. This can be accomplished only with a difunctional initiator such as $LiOSi(Ph)_2O(Ph)_2SiOLi$[59]. Crosslinking at higher temperatures may be accomplished with conventional peroxides.

4. The synthesis of copolymers from the cyclocarbosiloxanes and a study of their properties are needed. Both random and block copolymers can be synthesized. While the random copolymers can be synthesized just by mixing the monomers before reacting, the block copolymers may be synthesized by the sequence addition of the monomers. By this method both amorphous and crystalline regions in the polymer chains may be introduced by the proper selection of monomers.

5. The potential use of these crosslinked homopolymers and copolymers as medical implants must be investigated. Since essentially monodispersed polymers can be synthesized, the amount of low molecular weight materials that can be extracted after crosslinking will be negligible. This behavior is believed to be one of the reasons for the degradation of conventional silicone heart valve poppets.

6. The use of these crosslinked polymers as membranes for use in oxygenators should be investigated.

VITA

Balaraman Suryanarayanan was born on September 18, 1944 in Kumbakonam, India. He received his primary and secondary education in Madras, India. He received his college education from the University of Madras, in India, the University of Bombay, in India, and the University of Missouri-Rolla, in Rolla, Missouri. He received a Bachelor of Science degree in Chemistry from the University of Madras, in India, in August 1964. He received a Bachelor of Science degree in Chemical Technology from the University of Bombay, in India, in August 1966. He worked as a chemist in Philips India Ltd., in Poona, India during 1967-69.

He has been enrolled in the Graduate School of the University of Missouri-Rolla since June 1969 and received a Master of Science degree in Chemistry in May 1971. He has held a fellowship from the Graduate Center for Materials Research from July 1969 to the present.

APPENDIX A

CALCULATION OF MOLAR REFRACTIONS OF MONOMERS

Molar refraction is related to refractive index, molecular weight and density of the compound according to the following relationship:

$$MR = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}$$

where,

MR = molar refraction cm^3/mole

n = refractive index

M = molecular weight gm/mole

d = density $\frac{gm}{cm^3}$

Thus from the measurements of refractive index, the density of the compound molar refraction MR_{obs} can be obtained.

Molar refraction is also composed additively of bond and group refractions. Warrick,[60] and Vogel et al.[61] have listed the bond and group refractions in some organosilicon and carbon compounds, and the pertinent bond and group refractions are listed below.

Bond	Refractions cm^3/mole
Si-O	1.75
Si-C (aliphatic)	2.50
Si-C (aromatic)	2.56
$Si-CH_3$	7.57
$Si-C_6H_5$	27.39
C-C	1.296
C-H	1.674

Molar refractions can be calculated for the cyclic monomers from the above table. For example for cyclic A with the structure

$(Me)_2SiCH_2CH_2Si(Me)_2O$

$$MR\ (calcd) = 2(1.75) + 4(7.57) + 2(2.50) + 1.296 + 4(1.674)$$

$$= \underline{46.77}\ cm^3/mole$$

This value for molar refraction can be compared with that calculated from refractive index and density measurements. For example for cyclic A refractive index $n_D^{20} = 1.4179$ and density$^{20} = 0.8620$ at 20^o.

$$\therefore\ MR_{obs} = \frac{(1.4179)^2 - 1}{(1.4179)^2 + 2} \times \frac{160.3}{0.8620}\ \frac{g/mole}{g/cm^3}$$

$$= \underline{46.85}\ cm^3/mole$$

Comparisons of MR_{calcd} and MR_{obs} indicate cyclic A to be of high purity.

APPENDIX B

THE EXCHANGE OF CHLORO AND ETHOXY GROUPS UPON THE ADDITION OF DIMETHYLCHLOROSILANE TO VINYLDIMETHYLETHOXYSILANE

THE EXCHANGE OF CHLORO AND ETHOXY GROUPS UPON THE ADDITION OF DIMETHYLCHLOROSILANE TO VINYLDIMETHYLETHOXYSILANE

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SUMMARY

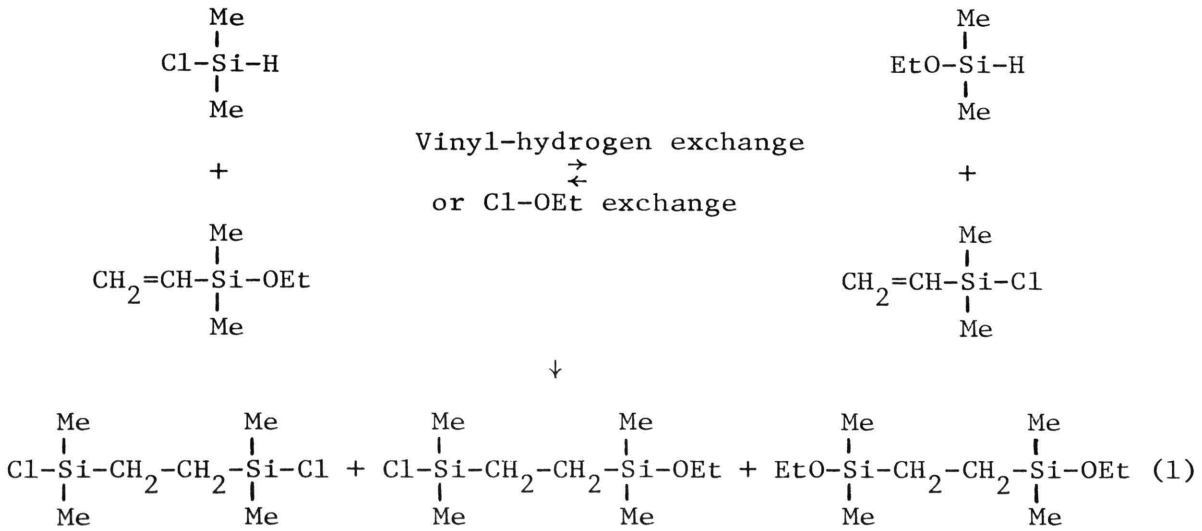
The addition of dimethylchlorosilane to vinyldimethylethoxysilane in the presence of chloroplatinic acid yielded 1,2-bis(dimethylchlorosilyl)ethane, 1-(dimethylchlorosilyl)-2-(dimethylethoxysilyl)ethane and 1,2-bis(dimethylethoxysilyl)ethane. The formation of three products is explained on the basis of chloro-ethoxy exchange reactions. Equilibration of the dimethylchlorosilane-vinyldimethylethoxysilane system was investigated using ^{1}H NMR and gas-liquid chromatography. The equilibrium constants indicated near random behavior for the substituent exchange.

INTRODUCTION

The synthesis of 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane $(Me)_2\overline{SiCH_2CH_2Si(Me)_2}O$ was previously carried out[1] by a chloroplatinic acid-catalyzed hydrosilation reaction between dimethylchlorosilane and vinyldimethylchlorosilane followed by the

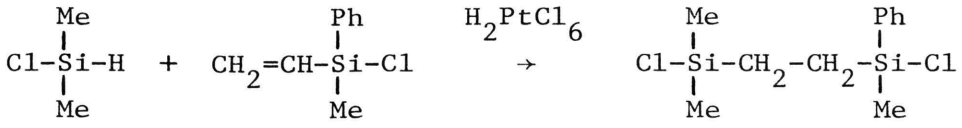
hydrolysis of the adduct and subsequent pyrolysis of the hydrolysate in the presence of a base. We have utilized the more readily available vinyldimethylethoxysilane in this synthesis, since the hydrolysis of the adduct and pyrolysis reaction yield the same cyclic compound. However the addition reaction yielded, in addition to the desired 1-(dimethylchlorosilyl)-2-(dimethylethoxysilyl)ethane, two other adducts which were identified as 1,2-bis(dimethylchlorosilyl)ethane and 1,2-bis-(dimethylethoxysilyl)ethane.

Redistribution reactions of organosilicon compounds are well known and have been the subject of several reviews[2,3,4]. Pitt and Skillern[5] first reported the exchange of vinyl groups and hydrogen on silicon atoms in the presence of chloroplatinic acid. The three products obtained in the present study can be explained by chloro-ethoxy exchange reactions among the reagents and products or by vinyl-hydrogen exchange (Eqns. 1 and 3). Therefore, a study was undertaken to determine the extent of these exchange reactions.

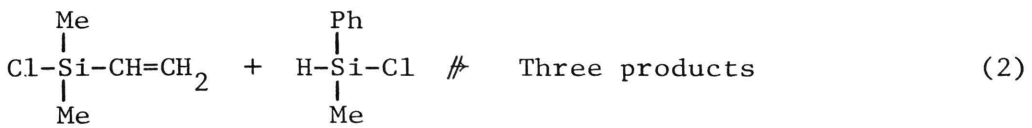


RESULTS AND DISCUSSION

Pitt and Skillern[5] carried out the addition of triethylsilane to vinyldimethylchlorosilane catalyzed by chloroplatinic acid and isolated three adducts, 1,2-bis-(dimethylchlorosilyl)ethane, 1-(triethylsilyl)-2-(dimethylchlorosilyl)ethane, and 1,2-bis(triethylsilyl)ethane. They explained the formation of the three products on the basis of vinyl-hydrogen ligand exchange between silicon atoms. In order to see if the vinyl-hydrogen exchange reaction is prevalent in our scheme, we carried out the addition of dimethylchlorosilane to phenylmethylvinylchlorosilane in the presence of chloroplatinic acid to obtain 1-(dimethylchlorosilyl)-2-(phenylmethylchlorosilyl)ethane in 90% yields. No other identifiable products were obtained. Had the vinyl-hydrogen ligand exchange been occurring, we would have expected two other products, 1,2-bis(dimethylchlorosilyl)ethane, and 1,2-bis(phenylmethylchlorosilyl)ethane in addition to 1-(dimethylchlorosilyl)-2-(phenylmethylchlorosilyl)ethane (Eqn. 2).



vinyl-hydrogen exchange β-adduct



(2)

Piccoli, et al.[1] reported that addition reactions of $ClSi(R)(R_1)H$ compounds to $CH_2=CHSi(R)(R_1)Cl$ compounds in the presence of chloroplatinic acid gave the β-adducts in high yields. These observations suggest that vinyl hydrogen ligand exchange reaction was not important for the formation of the products obtained in this study.

Unlike vinyl-hydrogen exchange, the chloro-ethoxy exchange reactions on silicon atoms do not require the presence of chloroplatinic acid. The chloro-ethoxy exchange reaction was independent of the presence or absence of chloroplatinic acid. Consequently, on mixing dimethylchlorosilane with vinyldimethylethoxysilane, it was possible to study the exchange reaction in the absence of the hydrosilation addition reaction. The exchange was followed by ^1H NMR, by observing the silyl proton signals of $(CH_3)_2Si(H)Cl$ and $(CH_3)_2Si(H)OEt$, the chemical shifts for the line protons being 294 and 282 Hz respectively, relative to $CHCl_3$. The relative amounts of dimethylchlorosilane and dimethylethoxysilane were measured by electronic integration of the two multiplets. Attempts to measure directly the amounts of all the components was not possible since the $Si-CH_3$ region of the spectra was too complex. Figure 1 shows the NMR pattern for the equilibration of 1/1 molar mixtures of dimethylchlorosilane and vinyldimethylethoxysilane at 28.5°. From the relative ratios of dimethylchlorosilane and dimethylethoxysilane at equilibrium, and by a material balance the equilibrium constants were calculated according to the relationship:

$$K = \frac{[(CH_3)_2Si(H)OEt][(CH_3)_2Si(Cl)CH=CH_2]}{[(CH_3)_2Si(H)Cl][(CH_3)_2Si(OEt)CH=CH_2]}$$

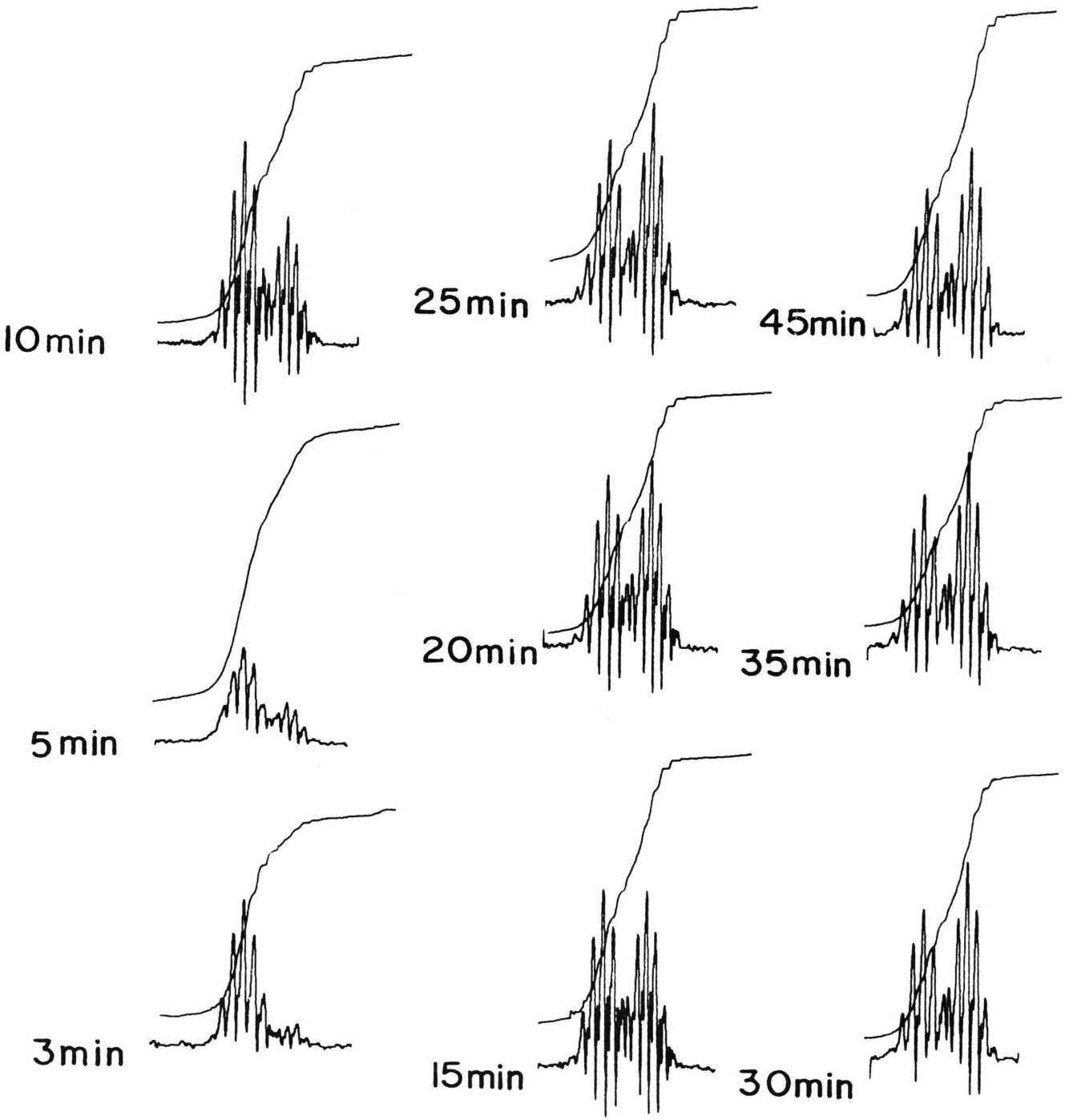


Figure 1. NMR Spectra of the Equilibration of 1/1 Molar Mixture of $(CH_3)_2Si(H)Cl$ and $(CH_3)_2Si(OEt)CH=CH_2$ at 28.5°

and are presented in Table 1.

GLC analyses of equilibrated mixtures (Table 2) agree well with NMR determinations. Equilibrium constants obtained in this study are near unity as expected for random exchange.

TABLE 1

EQUILIBRATION OF MIXTURES OF $(CH_3)_2Si(H)Cl$ AND $(CH_3)_2Si(OEt)CH=CH_2$ AT 28.5°C

Mole ratio (EtO/Cl)	Exchange(%) at[a] equilibrium	Equilibrium constant K
1/1	55.3	1.53
3/2	63.0	1.33
2/3	42.0	1.23

[a]Duplicate measurement led to % exchange at equilibrium within 0.4%

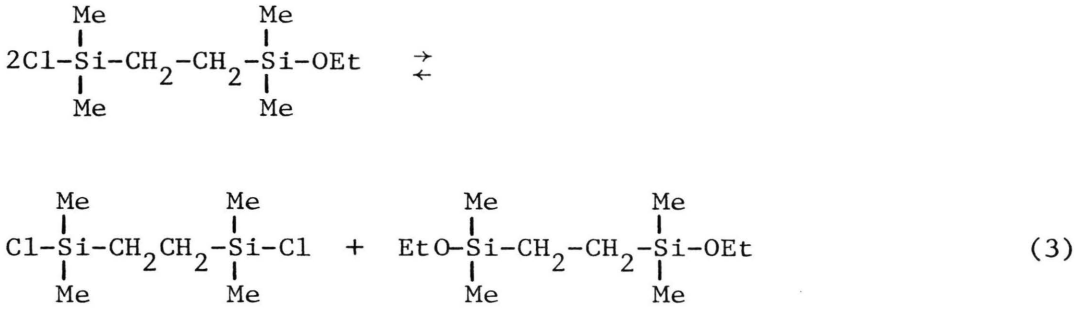
TABLE 2

NMR AND GLC ANALYSES ON THE 1/1 MOLAR MIXTURE OF $(CH_3)_2Si(H)Cl$ AND $(CH_3)_2Si(OEt)CH=CH_2$ EQUILIBRATED AT 28.5°

Component	Weight (%)	
	NMR	GLC
Dimethylchlorosilane	18.76	18.60
Dimethylethoxysilane	25.68	26.10
Vinyldimethylchlorosilane	29.60	30.20
Vinyldimethylethoxysilane	25.96	25.10

The rate of exchange of chloro and ethoxy groups for the equilibration of 1:1, 3:2 and 2:3 molar mixtures of dimethylchlorosilane and vinyldimethylethoxysilane at 28.5° is shown in Fig. 2. The figure shows that the exchange is rapid near room temperatures. When precautions were not taken to exclude atmospheric moisture, equilibration was complete in less than two minutes. Trace amounts of HCl formed by hydrolysis of the chlorosilane are known[6] to exhibit catalytic activity. Figure 2 also shows that the rate of equilibration was faster as the amount of ethoxysilane was increased.

The formation of the two symmetrical products, 1,2-bis(dimethylchlorosilyl)ethane and 1,2-bis(dimethylethoxysilyl)ethane, may also be explained by means of Eqn. 3.



$$2\,ClSi(Me)_2CH_2CH_2Si(Me)_2OEt \rightleftarrows ClSi(Me)_2CH_2CH_2Si(Me)_2Cl + EtOSi(Me)_2CH_2CH_2Si(Me)_2OEt \qquad (3)$$

This possibility was investigated by mixing equimolar amounts of the two symmetrical compounds in an NMR tube, and heating to 120° for several hours. NMR spectra showed the appearance of the multiplet due to $-CH_2CH_2-$ of the unsymmetrical compound, indicating the reverse reaction. However, no quantitative data on this reaction was obtained.

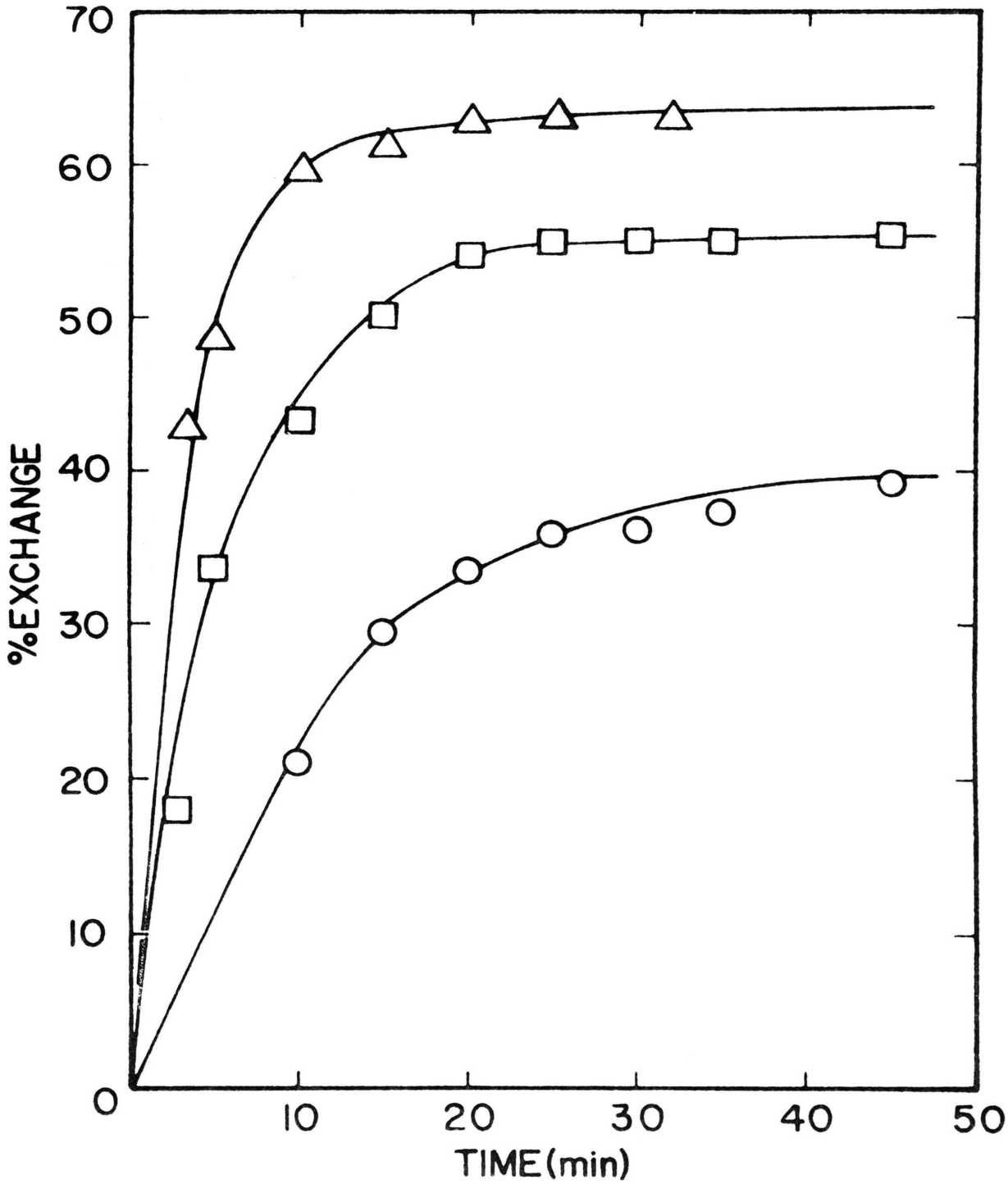


Figure 2. Rate of Equilibration of ○ 3/2 □ 1/1 and △ 2/3 Molar Mixtures of $(CH_3)_2Si(H)Cl$ and $(CH_3)_2Si(OEt)$-$CH=CH_2$ at 28.5°

It is thus evident that the chloro-ethoxy redistribution reactions before and after the hydrosilation addition reaction are responsible for the formation of the two symmetrical compounds in the preparative procedure.

EXPERIMENTAL

GLC analyses were performed with a Victoreen 4000 Series Chromatograph, equipped with a thermal conductivity detector and a 2m column of 10% SE 30 on Chromosorb W. NMR spectra were obtained with a Varian EM-360 spectrometer. Melting and boiling points are uncorrected. Elemental analysis was performed by Galbraith Laboratories, Knoxville, Tennessee.

Reagents. Specially purified dimethylchlorosilane was purchased from Pierce Chemical Company, Rockford, Illinois. Vinyldimethylethoxysilane was purchased from Alfa Inorganics, Cambridge, Massachusetts, and was purified by distillation. The catalyst for the addition reaction was prepared by dissolving 1.0 g of $H_2PtCl_6 \cdot 6H_2O$ in 19.3 g of isopropyl alcohol to give a 0.1 M solution. A 10 µl sample of the catalyst solution was equivalent to 10^{-6} mole Pt.

Phenylmethylvinylchlorosilane was prepared by a modification of the Grignard method employed by Curry[7]. The use of tetrahydrofuran as solvent increased the yield from 40 to 67%.

Addition of dimethylchlorosilane to vinyldimethylethoxysilane. To 26.0 g (0.2 mole) of vinyldimethylethoxysilane, 5 µl of chloroplatinic acid solution was added and the mixture was heated

to 75° under a nitrogen atmosphere. The mixture was stirred as 18.8 g (0.2 mole) of dimethylchlorosilane was added dropwise. The temperature rose to 120° and was maintained at that temperature by controlling the rate of addition. After the addition reaction was completed, the mixture was fractionated in a Nester-Faust auto annular still with a reflux ratio of 200/1 and the Teflon band spinning at 7200 rpm. 1,2-Bis(dimethylchlorosilyl)ethane was collected as a solid adduct at 109°/50 mm Hg. Recrystallization from n-pentane yielded the pure compound melting at 36°. An NMR spectrum of the adduct using carbon tetrachloride as the solvent and chloroform as the internal standard* showed the $Si-CH_3$ singlet at 24 Hz and the $-CH_2CH_2-$ singlet at 50 Hz. The second fraction collected at 113°/50 mm Hg was found by NMR analysis to be a mixture of 1,2-bis(dimethylchlorosilyl)ethane, 1,2-bis(dimethylethoxysilyl)-ethane and 1-(dimethylchlorosilyl)-2-(dimethylethoxysilyl)ethane. Repeated fractionation gave the unsymmetrical adduct in 70% purity. The NMR spectrum of this fraction showed a multiplet due to $-CH_2CH_2-$ group in the unsymmetrical adduct at 32 Hz. The third fraction, 1,2-bis(dimethylethoxysilyl)ethane, was collected at 116°/50 mm Hg. (n_D^{20} 1.4205, Found: C, 51.00; H, 11.08; Si, 23.97. Calcd.: C, 51.19; H, 11.18; Si, 23.97). The NMR spectrum of the compound showed the $-CH_2CH_2$ singlet at 25 Hz and the $Si-CH_3$ singlet at 0 Hz.

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*Chloroform was used as the internal standard rather than tetramethylsilane because of the extremely close chemical shifts of $Si-CH_3$ between these adducts and tetramethylsilane.

Equilibration of dimethylchlorosilane with vinyldimethylethoxylsilane. The exchange of chloro and ethoxy groups during the equilibration of dimethylchlorosilane with vinyldimethylethoxysilane was determined as follows: measured amounts of the two reactants from previously calibrated syringes were transferred into an NMR tube in a polyethylene glove bag. A steady flow of purified inert gas (N_2 or Ar) was maintained inside the glove bag. The NMR tube was sealed and the reactants were mixed, the time of mixing being taken as zero time. The NMR tube was immediately transferred to the probe of the NMR spectrometer maintained at a constant temperature of 28.5°. The spectra between 270 and 310 Hz were scanned with respect to time. Electronic integration of the multiplets yielded the relative ratios of dimethylchlorosilane and dimethylethosyxilane.

GLC analyses on the equilibrated mixtures were performed on samples taken from the NMR tube. The elapsed time between NMR analysis and GLC analysis was usually about 3 hours. GLC analysis showed four peaks corresponding to dimethylchlorosilane (b.p. 36°), dimethylethoxysilane (b.p. 54°), vinyldimethylchlorosilane (b.p. 83-84°), and vinyldimethylethoxysilane (b.p. 99°). The peaks due to dimethylchlorosilane and vinyldimethylethoxysilane were identified by comparison with pure samples and assignments of the chromatographic peaks due to dimethylethoxysilane and vinyldimethylchlorosilane were made from their boiling point sequence and were checked by material balance.

ACKNOWLEDGEMENTS

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APPENDIX C

FIRST ORDER PLOTS OF POLYMERIZATION OF CYCLICS B, C, D AND E AT AN INITIATOR CONCENTRATION OF 3.0×10^{-3} MOLE/LITER, THF CONCENTRATION OF 0.787 MOLE/LITER AND AT 31.7°

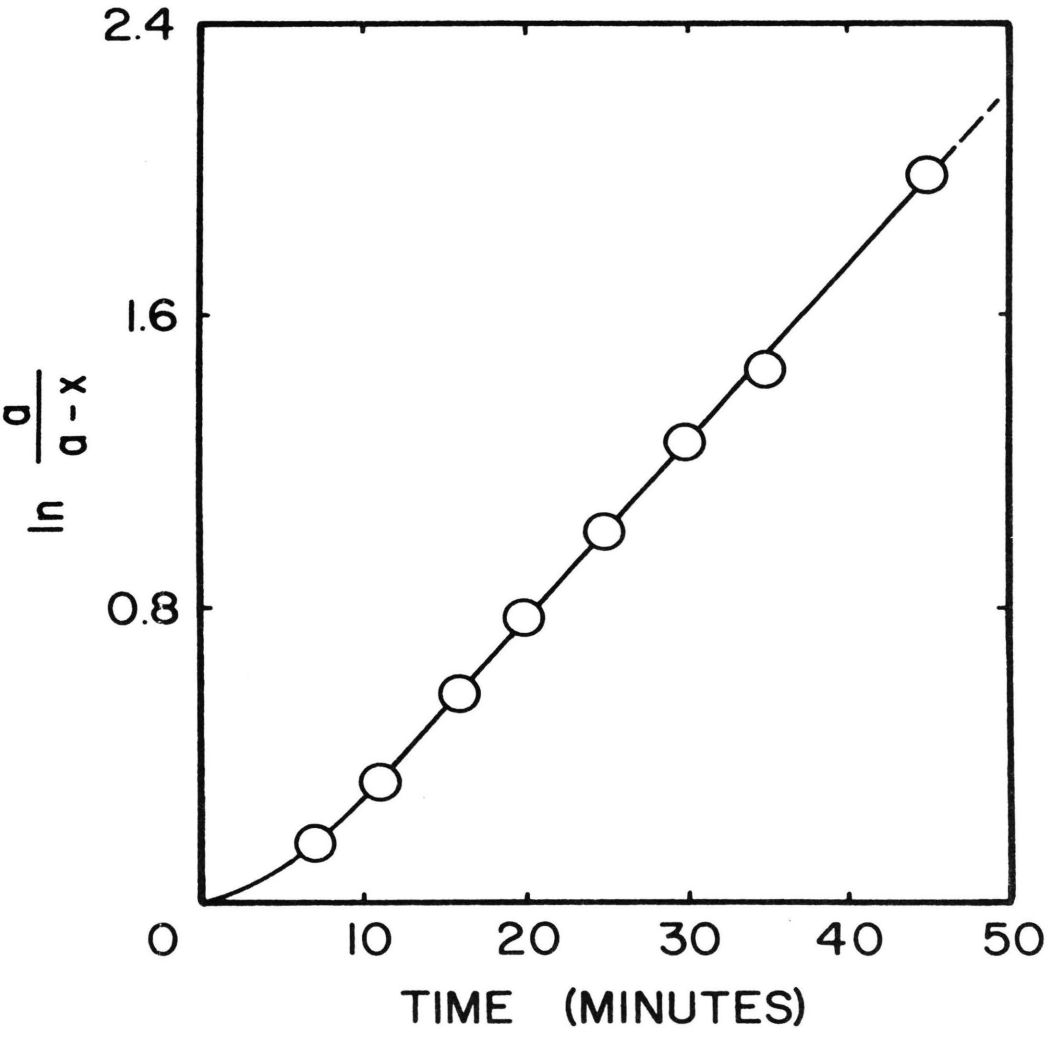

Figure 11. First Order Plot for Polymerization of Cyclic B

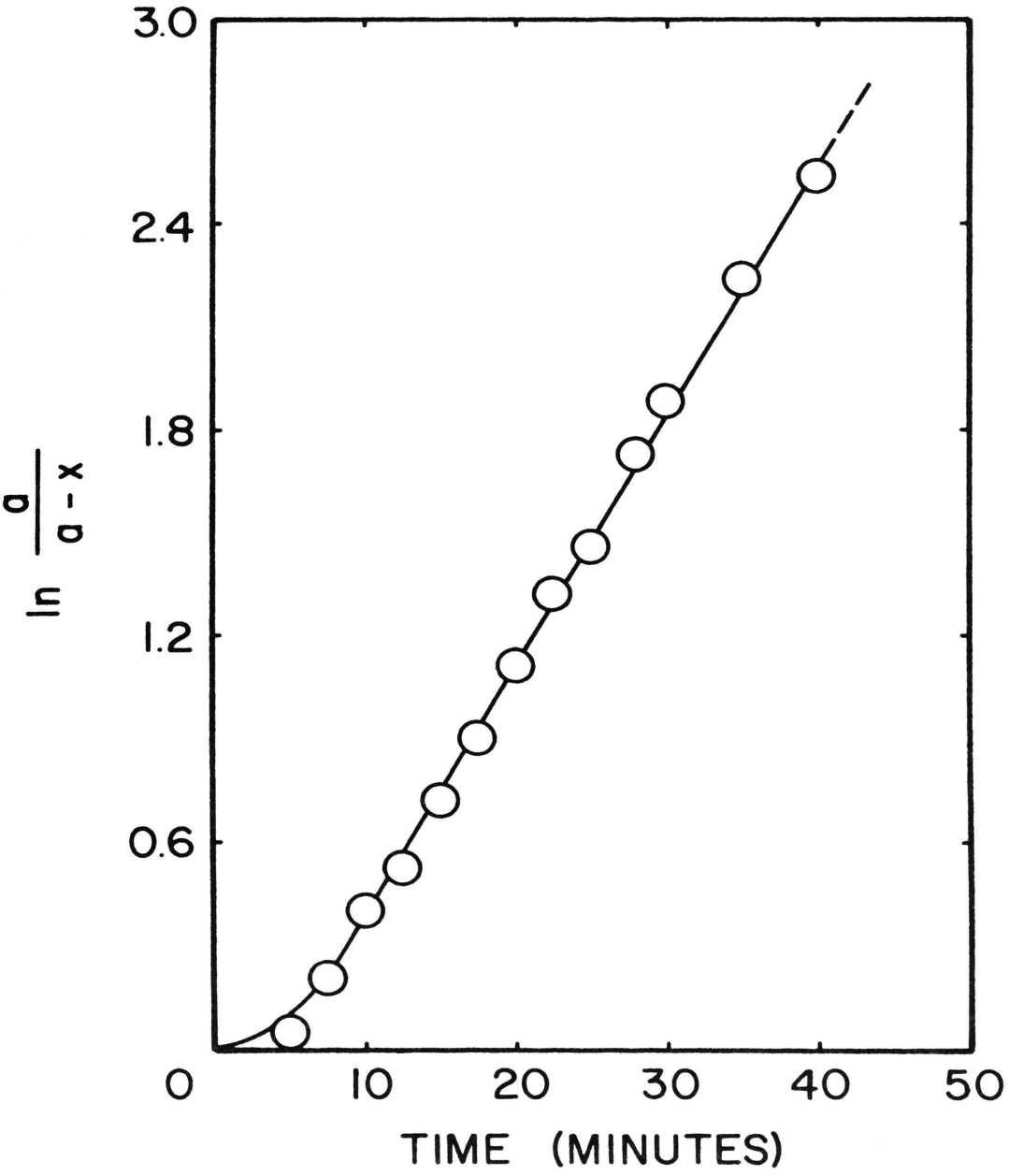

Figure 12. First Order Plot for Polymerization of Cyclic C

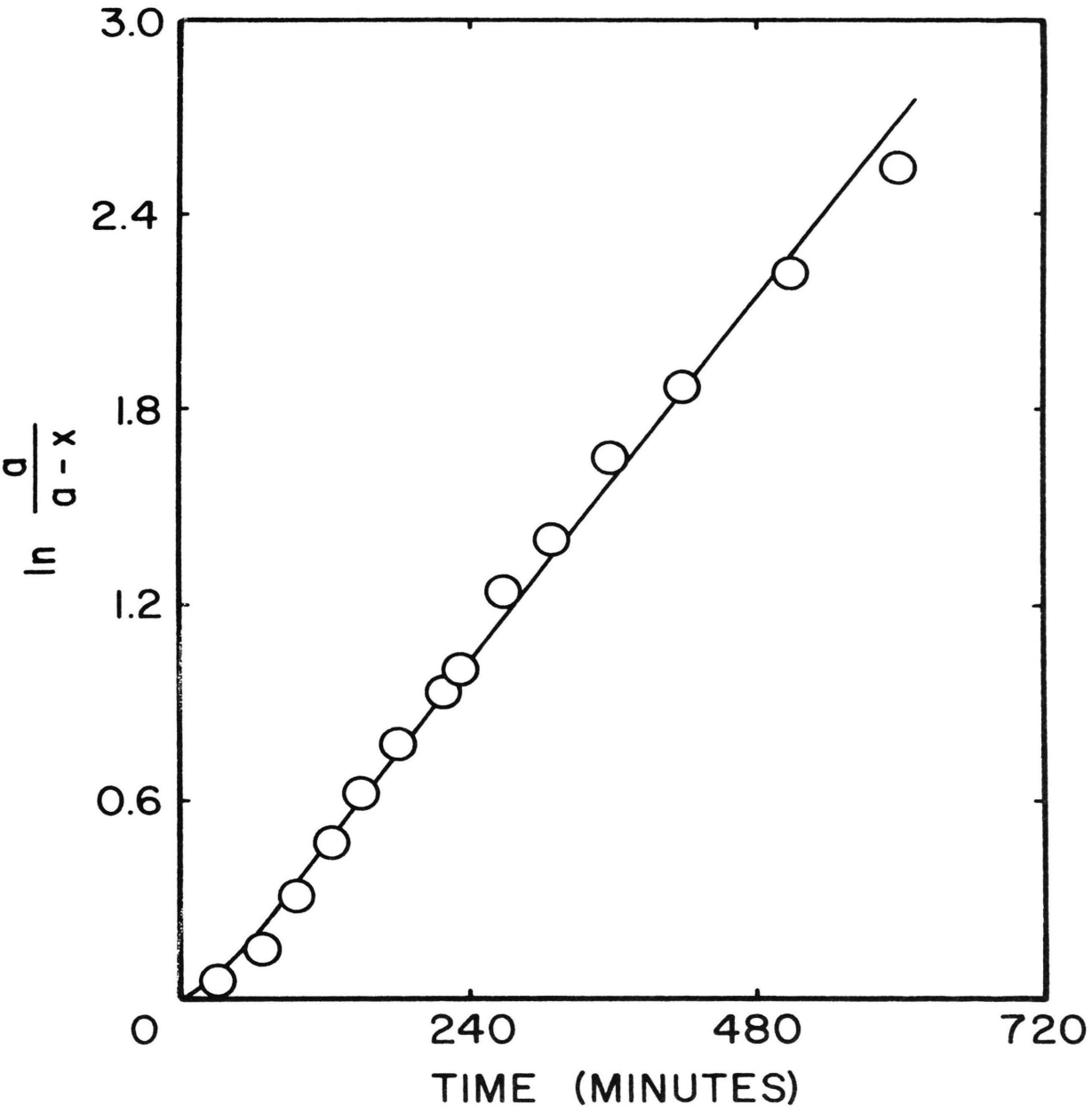

Figure 13. First Order Plot for Polymerization of Cyclic D

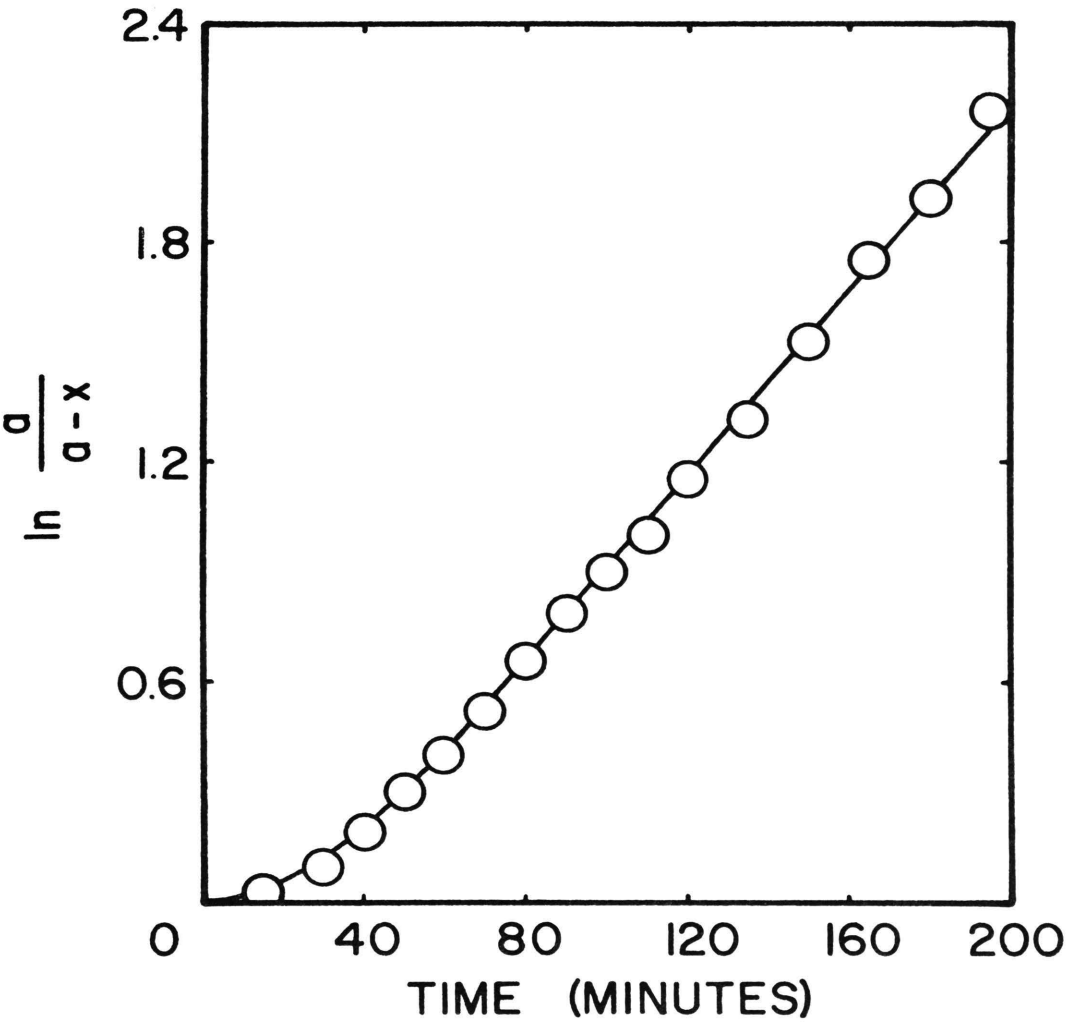

Figure 14. First Order Plot for Polymerization of Cyclic E

APPENDIX D

TABULATION OF CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC A AT 31.7°, AS A FUNCTION OF THF CONCENTRATION AT AN INITIATOR CONCENTRATION OF 3.0×10^{-3} MOLE/LITER

TABLE XIV

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC A AT THF CONCENTRATION OF 0.214 MOLE/LITER

Time Minutes	Area		% Conversion	$\ln \frac{a}{a-x}$
	Monomer	Polymer		
10.0	10.00	0.20	2.0	0.02
20.0	9.25	0.55	5.6	0.06
30.0	9.50	1.35	12.5	0.13
40.0	6.65	1.90	22.2	0.25
50.0	6.00	3.10	34.1	0.42
60.0	5.20	4.00	43.5	0.52
70.0	4.65	4.85	51.2	0.72
80.0	4.10	6.20	60.2	0.92
91.0	2.70	5.90	68.6	1.16
105.0	2.50	7.00	73.7	1.34
120.0	1.95	8.30	80.8	1.65
135.0	1.40	7.75	84.8	1.88
150.0	1.20	8.70	88.0	2.12
167.2	0.90	8.20	90.2	2.32
180.0	0.75	8.55	92.0	2.53

TABLE XV

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC A AT THF CONCENTRATION OF 0.428 MOLE/LITER

Time Minutes	Area		% Conversion	$\ln \frac{a}{a-x}$
	Monomer	Polymer		
5.0	10.20	0.40	3.8	0.04
10.0	10.80	1.50	12.2	0.13
15.0	9.45	2.60	21.6	0.24
20.0	7.60	3.60	32.1	0.39
25.0	7.20	5.30	42.4	0.55
30.0	6.40	6.00	48.4	0.66
35.0	5.30	7.90	59.8	0.91
40.0	4.50	8.00	64.0	1.02
45.0	3.30	8.55	72.2	1.28
50.0	3.00	10.10	77.1	1.47
55.0	2.20	9.70	81.5	1.69
60.0	2.00	11.40	85.1	1.90
70.0	1.35	11.00	89.1	2.22
80.0	0.90	10.45	92.1	2.54

TABLE XVI

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC A AT THF CONCENTRATION OF 0.787 MOLE/LITER

Time Minutes	Area		% Conversion	$\ln \frac{a}{a-x}$
	Monomer	Polymer		
3.0	10.10	0.60	5.6	0.06
5.0	9.60	1.10	10.3	0.11
7.5	8.20	2.10	20.4	0.23
10.0	7.25	3.15	30.3	0.36
12.5	6.70	4.60	40.7	0.52
15.0	5.90	6.50	52.4	0.74
17.5	4.90	7.00	58.8	0.89
20.0	4.45	8.70	66.2	1.09
22.5	3.65	9.30	71.8	1.27
25.0	2.80	9.00	76.3	1.44
30.0	2.20	10.70	82.9	1.77
35.0	1.35	12.30	90.1	2.31
40.0	1.00	12.20	92.4	2.58
45.0	0.70	11.20	94.1	2.83

TABLE XVII

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC A AT THF CONCENTRATION OF 1.574 MOLE/LITER

Time Minutes	Area		% Conversion	$\ln \frac{a}{a-x}$
	Monomer	Polymer		
2.5	8.85	1.50	14.5	0.16
4.0	7.50	2.70	26.5	0.31
5.1	7.80	5.20	40.0	0.51
6.4	5.70	6.20	52.1	0.74
7.5	5.00	7.60	60.3	0.92
8.6	4.15	7.90	65.6	1.07
10.2	2.70	8.70	76.3	1.44
12.5	2.00	10.70	84.2	1.85
15.0	1.20	9.50	88.8	2.19
17.5	0.90	11.70	92.9	2.65
20.0	0.60	12.40	95.4	3.08

APPENDIX E

TABULATION OF CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC A AT 31.7°, AS A FUNCTION OF INITIATOR CONCENTRATION AT CONSTANT THF CONCENTRATIONS

TABLE XVIII

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC A AT AN INITIATOR CONCENTRATION OF 0.6×10^{-3} MOLE/LITER[a]

Time Minutes	Area		% Conversion	$\ln \frac{a}{a-x}$
	Monomer	Polymer		
2.5	10.80	1.20	10.0	0.11
7.5	7.40	2.20	22.9	0.26
10.0	7.90	4.30	35.2	0.43
12.5	6.50	6.50	50.0	0.69
15.0	5.10	8.20	61.7	0.96
17.5	3.60	8.60	70.5	1.22
20.0	2.90	10.10	77.7	1.50
25.0	1.50	10.40	87.4	2.07
30.0	0.90	11.60	92.8	2.63
35.0	0.50	11.60	95.8	3.17

a. [THF] = 1.574 mole/liter

TABLE XIX

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC A AT AN INITIATOR CONCENTRATION OF 1.2×10^{-3} MOLE/LITER[a]

Time Minutes	Area		% Conversion	$\ln \frac{a}{a-x}$
	Monomer	Polymer		
2.66	8.80	1.10	11.1	0.12
5.00	9.20	2.30	20.0	0.22
7.66	7.40	4.90	39.8	0.51
10.00	5.20	6.50	55.6	0.81
12.50	4.10	8.50	67.5	1.12
15.00	2.85	9.30	76.5	1.45
17.50	2.00	10.10	83.5	1.80
20.20	1.40	10.90	88.6	2.17
22.50	1.10	11.90	91.5	2.47
25.00	0.80	11.10	93.3	2.70
30.00	0.50	12.00	96.0	3.22

a. [THF] = 1.574 mole/liter

TABLE XX

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC A AT AN INITIATOR CONCENTRATION OF 6.0×10^{-3} MOLE/LITER[a]

Time Minutes	Area		% Conversion	$\ln \frac{a}{a-x}$
	Monomer	Polymer		
2.50	10.20	2.00	16.4	0.18
3.75	8.90	2.90	24.6	0.28
5.00	7.30	4.40	37.6	0.47
6.33	5.50	5.70	50.9	0.71
7.50	4.80	7.30	60.3	0.92
8.75	3.60	8.20	69.5	1.19
10.00	2.75	8.70	76.0	1.43
11.25	2.30	9.80	81.0	1.66
12.50	1.80	9.90	84.6	1.87
13.75	1.55	11.10	87.8	2.10
17.50	0.70	10.70	93.9	2.80

a. [THF] = 1.574 mole/liter

TABLE XXI

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC A AT AN INITIATOR CONCENTRATION OF 12.0×10^{-3} MOLE/LITER[a]

Time Minutes	Area		% Conversion	$\ln \frac{a}{a-x}$
	Monomer	Polymer		
2.50	9.80	1.80	15.5	0.17
3.75	8.20	2.60	24.1	0.28
5.00	6.30	4.30	40.6	0.52
6.25	5.40	5.80	51.7	0.73
7.50	4.35	7.10	62.0	0.97
8.75	3.70	9.40	71.8	1.27
10.40	2.50	10.10	80.2	1.62
13.90	1.10	10.30	90.4	2.34
15.00	0.90	10.40	92.0	2.53
17.50	0.50	10.60	95.5	3.10
20.00	0.35	11.00	96.9	3.47

a. [THF] = 1.574 mole/liter

TABLE XXII

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC A AT AN INITIATOR CONCENTRATION OF 24.0×10^{-3} MOLE/LITER[a]

Time Minutes	Area		% Conversion	$\ln \frac{a}{a-x}$
	Monomer	Polymer		
2.50	10.60	1.80	14.5	0.16
3.75	7.50	2.60	25.7	0.30
5.00	7.20	4.20	36.8	0.46
6.25	5.70	5.80	50.4	0.70
7.50	4.30	6.75	61.1	0.94
8.75	3.30	7.80	70.3	1.21
10.10	2.75	9.30	77.2	1.48
11.25	2.30	10.10	81.5	1.69
12.70	1.65	10.90	86.9	2.03
13.83	1.30	11.00	89.4	2.24
15.00	0.95	10.70	91.9	2.51
17.50	0.60	11.50	95.1	3.02
20.00	0.35	11.30	97.0	3.51

a. [THF] = 1.574 mole/liter

TABLE XXIII

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC A AT AN INITIATOR CONCENTRATION OF 0.6×10^{-3} MOLE/LITER[a]

Time Minutes	Area		% Conversion	$\ln \frac{a}{a-x}$
	Monomer	Polymer		
3.0	12.20	0.60	4.7	0.05
5.0	9.90	0.70	6.6	0.07
10.0	10.20	1.75	14.6	0.16
15.0	8.10	2.70	25.0	0.29
20.0	7.30	4.50	38.1	0.48
25.0	6.10	6.00	49.6	0.69
30.0	4.20	6.60	61.1	0.94
35.0	3.60	7.85	68.6	1.16
40.6	3.20	10.30	76.3	1.44
50.3	1.90	10.40	84.6	1.87
60.0	1.00	9.80	90.7	2.38
70.0	0.70	10.40	93.7	2.77
80.0	0.50	9.50	95.0	3.00

a. [THF] = 0.787 mole/liter

TABLE XXIV

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC A AT AN INITIATOR CONCENTRATION OF 1.2×10^{-3} MOLE/LITER[a]

Time Minutes	Area		% Conversion	$\ln \frac{a}{a-x}$
	Monomer	Polymer		
3.0	10.70	0.80	7.0	0.07
5.0	9.90	1.15	10.4	0.11
10.0	8.50	2.66	23.4	0.27
16.6	6.10	4.90	44.5	0.59
20.0	4.80	6.00	55.6	0.81
25.0	3.80	7.90	67.5	1.12
30.4	2.70	8.90	76.7	1.46
35.0	2.20	9.30	80.9	1.66
40.0	1.70	10.20	85.7	1.95
50.0	0.90	10.70	92.2	2.55
60.0	0.60	11.30	95.0	3.00

a. [THF] = 0.787 mole/liter

TABLE XXV

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC A AT AN INITIATOR CONCENTRATION OF 6.0×10^{-3} MOLE/LITER[a]

Time Minutes	Area		% Conversion	$\ln \frac{a}{a-x}$
	Monomer	Polymer		
2.75	10.80	0.90	7.7	0.08
5.00	9.80	1.50	13.3	0.14
7.83	9.90	2.70	21.4	0.24
10.00	8.40	3.50	29.4	0.35
15.00	5.60	5.80	50.9	0.71
17.50	4.50	6.70	59.8	0.91
20.00	3.60	7.60	67.9	1.14
25.20	2.65	9.60	78.4	1.53
30.00	1.75	10.00	85.1	1.90
35.00	1.30	11.00	89.4	2.24
40.00	0.90	11.50	92.7	2.62
45.00	0.60	10.00	94.3	2.87

a. [THF] = 0.787 mole/liter

TABLE XXVI

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC A AT AN INITIATOR CONCENTRATION OF 12.0×10^{-3} MOLE/LITER[a]

Time Minutes	Area		% Conversion	$\ln \frac{a}{a-x}$
	Monomer	Polymer		
2.50	10.10	0.75	6.9	0.07
5.00	9.90	1.40	12.4	0.13
7.50	7.90	2.10	21.0	0.24
10.00	8.00	3.45	30.1	0.36
12.50	6.30	4.15	39.7	0.51
15.00	5.55	5.55	50.0	0.69
20.00	3.45	7.15	67.5	1.12
25.00	3.15	9.70	75.5	1.41
30.00	1.70	9.30	84.5	1.86
35.00	1.40	11.40	89.1	2.22
40.00	0.80	10.70	93.0	2.66
45.00	0.60	10.80	94.7	2.94

a. [THF] = 0.787 mole/liter

TABLE XXVII

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC A AT AN INITIATOR CONCENTRATION OF 0.6×10^{-3} MOLE/LITER[a]

Time Minutes	Area		% Conversion	$\ln \frac{a}{a-x}$
	Monomer	Polymer		
10.0	10.95	0.35	3.1	0.03
20.00	9.20	0.75	7.5	0.08
30.00	10.30	2.20	17.6	0.19
40.0	8.40	3.80	31.2	0.37
45.0	7.50	4.60	38.0	0.48
52.5	6.70	5.40	44.6	0.59
60.0	5.00	5.80	53.7	0.77
70.0	4.90	7.90	61.7	0.96
80.0	3.90	8.60	68.8	1.17
90.0	3.30	9.50	74.2	1.36
100.5	2.70	10.00	78.7	1.55
114.3	1.90	9.80	83.8	1.82
120.8	1.90	11.90	86.2	1.98
137.2	1.20	11.70	90.7	2.38
150.0	0.90	11.20	92.6	2.60
165.0	0.70	10.60	93.8	2.78

a. [THF] = 0.428 mole/liter

TABLE XXVIII

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC A AT AN INITIATOR CONCENTRATION OF 1.2×10^{-3} MOLE/LITER[a]

Time Minutes	Area		% Conversion	$\ln \frac{a}{a-x}$
	Monomer	Polymer		
10.5	11.30	0.70	5.8	0.06
16.8	9.90	1.30	11.6	0.12
22.5	8.80	2.15	19.6	0.22
30.7	7.20	3.35	31.8	0.38
37.5	6.85	5.70	45.4	0.61
45.0	5.30	6.55	55.3	0.81
52.5	4.05	6.90	63.0	1.00
60.0	3.35	7.20	68.3	1.15
70.0	2.95	9.30	75.9	1.42
80.0	1.95	9.30	82.7	1.75
90.0	1.75	10.40	85.6	1.94
105.0	1.00	9.80	90.7	2.38
120.0	0.80	12.00	93.8	2.77
135.0	0.60	11.70	95.1	3.02

a. [THF] = 0.428 mole/liter

TABLE XXIX

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC A AT AN INITIATOR CONCENTRATION OF 6.0×10^{-3} MOLE/LITER[a]

Time Minutes	Area		% Conversion	$\ln \frac{a}{a-x}$
	Monomer	Polymer		
5.0	11.00	0.70	6.0	0.06
10.0	10.35	1.25	10.8	0.11
20.0	10.20	3.70	26.6	0.31
30.0	5.60	5.60	50.0	0.69
40.0	4.30	8.10	65.3	1.06
50.0	2.60	8.60	76.8	1.46
61.3	1.80	9.90	84.6	1.87
70.0	1.45	11.20	88.5	2.16
80.0	0.80	8.80	91.7	2.49

a. [THF] = 0.428 mole/liter

TABLE XXX

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC A AT AN INITIATOR CONCENTRATION OF 12.0×10^{-3} MOLE/LITER[a]

Time Minutes	Area		% Conversion	$\ln \frac{a}{a-x}$
	Monomer	Polymer		
5.0	10.30	0.65	5.9	0.06
10.0	10.10	1.40	12.2	0.13
20.0	8.20	3.15	27.8	0.33
36.7	5.60	5.35	48.9	0.67
40.0	4.05	7.45	64.8	1.04
50.0	2.30	7.35	76.2	1.44
60.0	1.70	8.00	82.5	1.74
70.0	1.30	9.40	87.9	2.11
80.0	0.90	9.60	91.4	2.45
90.0	0.60	10.00	94.3	2.87

a. [THF] = 0.428 mole/liter

TABLE XXXI

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC A AT AN INITIATOR CONCENTRATION OF 0.6×10^{-3} MOLE/LITER[a]

Time Minutes	Area		% Conversion	$\ln \frac{a}{a-x}$
	Monomer	Polymer		
15.0	9.50	0.10	1.0	0.01
30.0	9.10	0.40	4.2	0.04
45.0	9.80	1.10	10.1	0.11
60.0	7.80	2.10	26.9	0.31
75.0	6.90	3.60	34.3	0.42
90.0	6.35	4.85	43.3	0.57
105.0	4.80	5.40	52.9	0.75
120.0	4.20	6.50	60.7	0.93
135.0	3.50	7.10	67.0	1.11
150.0	2.55	6.70	72.4	1.29
165.0	2.10	7.50	78.1	1.52
180.0	1.90	8.10	81.0	1.66
195.0	1.70	8.90	84.0	1.83
210.0	1.45	9.60	86.8	2.03
240.0	0.85	8.60	91.0	2.40
270.0	0.70	9.50	93.1	2.68

a. [THF] = 0.214 mole/liter

TABLE XXXII

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC A AT AN INITIATOR CONCENTRATION OF 1.2×10^{-3} MOLE/LITER[a]

Time Minutes	Area		% Conversion	$\ln \frac{a}{a-x}$
	Monomer	Polymer		
15.0	10.10	0.25	2.4	0.02
22.5	10.20	0.50	4.7	0.05
30.0	8.20	0.80	8.9	0.09
45.0	7.80	2.00	20.4	0.23
60.0	6.40	3.00	31.9	0.38
70.0	5.70	4.10	41.8	0.54
80.0	5.20	5.20	50.0	0.69
90.5	4.20	5.40	56.3	0.83
100.0	3.70	6.20	62.6	0.98
110.0	2.95	6.05	67.2	1.12
120.0	3.05	7.30	70.5	1.22
133.3	2.50	8.00	76.2	1.44
150.0	2.40	9.80	80.3	1.63
180.0	1.30	8.80	87.1	2.03
221.7	0.90	10.10	91.8	2.50
240.0	0.70	10.40	93.7	2.77

a. [THF] = 0.214 mole/liter

TABLE XXXIII

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC A AT AN INITIATOR CONCENTRATION OF 6.0×10^{-3} MOLE/LITER[a]

Time Minutes	Area		% Conversion	$\ln \frac{a}{a-x}$
	Monomer	Polymer		
10.0	9.85	0.65	6.2	0.06
20.5	9.60	1.30	11.9	0.13
30.0	9.40	2.00	17.5	0.19
40.0	8.70	3.00	25.6	0.30
51.0	6.80	4.40	39.3	0.50
60.0	6.90	5.30	43.4	0.57
70.0	5.90	6.80	53.5	0.77
80.0	4.50	6.60	59.5	0.91
90.0	3.30	6.80	67.3	1.12
105.3	3.00	8.90	74.8	1.38
120.0	2.10	9.50	81.9	1.71
135.0	1.75	10.65	85.9	1.96
150.0	1.35	10.10	88.2	2.14

a. [THF] = 0.214 mole/liter

APPENDIX F

TABULATION OF CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC A AT 31.7° AS A FUNCTION OF WATER CONCENTRATION

TABLE XXXIV

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC A AT WATER CONCENTRATION OF 1.1×10^{-3} MOLE/LITER[a,b]

Time Minutes	Area		% Conversion	$\ln \frac{a}{a-x}$
	Monomer	Polymer		
10.0	9.85	0.25	2.5	0.03
20.0	10.80	0.60	5.3	0.05
30.0	9.40	1.20	11.3	0.12
43.7	8.10	2.20	21.4	0.24
50.0	8.55	3.20	27.2	0.32
60.0	7.35	4.25	36.6	0.46
70.0	6.15	4.95	44.6	0.59
80.0	4.90	5.35	52.2	0.74
90.0	4.70	7.00	59.8	0.91
100.0	3.90	7.45	65.6	1.07
110.0	3.40	8.30	70.9	1.24
120.0	2.85	8.25	74.3	1.36
135.5	2.20	8.90	80.2	1.62
150.0	1.85	10.30	85.0	1.90
180.0	1.15	10.20	89.9	2.29
195.0	1.00	11.40	91.9	2.52
210.0	0.80	11.10	93.3	2.70

a. [THF] = 0.214 mole/liter
b. [Initiator] = 2.4×10^{-3} mole/liter

TABLE XXXV

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC A AT WATER CONCENTRATION OF 8.7×10^{-3} MOLE/LITER[a,b]

Time Minutes	Area		% Conversion	$\ln \frac{a}{a-x}$
	Monomer	Polymer		
10.0	11.00	0.25	2.2	0.02
20.0	11.65	0.45	3.7	0.04
30.0	11.30	0.65	5.4	0.06
45.0	10.55	1.15	9.8	0.10
60.0	10.00	2.05	17.0	0.19
75.0	8.80	3.35	27.6	0.32
90.0	7.30	4.90	40.1	0.51
106.7	5.60	5.60	50.0	0.69
120.0	5.00	6.60	56.9	0.84
135.0	4.30	8.65	66.8	1.10
150.0	3.65	10.00	73.3	1.32
165.0	2.80	10.10	78.3	1.53
180.0	2.40	10.65	81.6	1.69
196.0	1.90	10.40	84.6	1.87
210.0	1.70	10.60	86.9	2.03
225.0	1.40	11.35	89.0	2.20
240.0	1.10	10.75	91.5	2.47
270.0	0.75	10.30	93.3	2.70

a. [THF] = 0.214 mole/liter
b. [Initiator] = 2.4×10^{-3} mole/liter

TABLE XXXVI

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC A AT WATER CONCENTRATION OF 1.0×10^{-3} MOLE/LITER[a,b]

Time Minutes	Area		% Conversion	$\ln \frac{x}{a-x}$
	Monomer	Polymer		
2.50	10.60	1.80	14.5	0.16
3.75	7.50	2.60	25.7	0.30
5.00	7.20	4.20	36.8	0.46
6.25	5.70	5.80	50.4	0.70
7.50	4.30	6.75	61.1	0.94
8.75	3.30	7.80	70.3	1.21
10.10	2.75	9.30	77.2	1.48
11.25	2.30	10.10	81.5	1.69
12.70	1.65	10.90	86.9	2.03
13.83	1.30	11.00	89.4	2.24
15.00	0.95	10.70	91.9	2.51
17.50	0.60	11.50	95.1	3.02
20.00	0.35	11.30	97.0	3.51

a. [THF] = 1.574 mole/liter
b. [Initiator] = 24.0×10^{-3} mole/liter

TABLE XXXVII

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC A AT WATER CONCENTRATION OF 25.0×10^{-3} MOLE/LITER[a,b]

Time Minutes	Area		% Conversion	$\ln \frac{a}{a-x}$
	Monomer	Polymer		
2.50	5.2	0.55	9.6	0.10
4.00	8.3	2.10	20.2	0.23
5.16	7.6	3.35	30.6	0.37
7.50	5.0	5.20	51.0	0.71
8.75	3.4	5.40	61.4	0.95
10.00	3.0	7.20	70.6	1.22
12.00	1.5	6.80	81.9	1.71
15.00	0.9	7.20	88.9	2.20
17.50	0.8	10.20	92.7	2.62
20.00	0.4	9.90	96.1	3.25

a. [THF] = 1.574 mole/liter
b. [Initiator] = 24.0×10^{-3} mole/liter

APPENDIX G

TABULATION OF CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC MONOMERS AT 20°, 31.7° and 40° AND AT CONSTANT CONCENTRATIONS OF MONOMERS, INITIATOR AND THF

TABLE XXXVIII

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC A AT 20°

Time Minutes	Area		% Conversion	$\ln \frac{a}{a-x}$
	Monomer	Polymer		
15.0	8.70	1.30	13.0	0.14
22.5	9.60	2.20	18.6	0.21
30.0	8.10	2.90	26.4	0.31
40.0	6.60	4.00	37.7	0.47
50.0	5.85	5.00	46.1	0.62
60.0	4.00	5.40	57.5	0.86
70.0	3.60	6.90	65.7	1.07
80.0	2.95	8.60	74.5	1.37
90.0	2.30	8.65	79.0	1.56
105.0	1.60	8.40	84.0	1.83
120.0	1.10	9.50	89.6	2.27

TABLE XXXIX

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC A AT 31.7°

Time Minutes	Area		% Conversion	$\ln \frac{a}{a-x}$
	Monomer	Polymer		
6.0	8.40	0.75	8.2	0.09
10.0	6.90	1.90	21.6	0.24
15.0	5.30	4.20	44.2	0.58
20.0	4.00	6.20	60.8	0.94
25.0	2.75	7.60	73.4	1.32
30.0	2.20	9.40	81.1	1.67
35.0	1.30	8.80	87.2	2.06
40.0	0.90	8.20	90.2	2.32
45.0	0.60	8.60	93.4	2.72
60.0	0.55	10.00	94.8	2.96

TABLE XL

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC A AT 40°

Time Minutes	Area		% Conversion	$\ln \frac{a}{a-x}$
	Monomer	Polymer		
3.0	9.90	1.10	10.0	0.11
4.0	8.50	1.45	14.6	0.16
5.0	6.70	2.70	28.7	0.34
10.0	4.50	5.00	52.6	0.75
15.0	2.70	6.20	69.5	1.19
20.0	1.60	8.40	84.0	1.83
25.0	1.20	9.70	89.0	2.21
30.0	0.70	9.00	92.8	2.63

TABLE XLI

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC B AT 20°

Time Minutes	Area		% Conversion	$\ln \frac{a}{a-x}$
	Monomer	Polymer		
20.0	9.70	1.50	13.4	0.14
30.0	9.90	2.60	20.8	0.23
45.0	10.20	3.90	27.7	0.32
60.0	8.00	4.70	37.0	0.46
75.0	6.90	6.60	48.9	0.67
90.0	6.70	8.10	55.1	0.80
106.7	5.40	8.70	61.7	0.96
131.7	2.90	5.50	65.5	1.06
150.0	3.30	9.80	75.0	1.39

TABLE XLII

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC B AT 31.7°

Time Minutes	Area		% Conversion	$\ln \frac{a}{a-x}$
	Monomer	Polymer		
5.33	7.60	1.05	12.1	0.13
10.00	7.95	1.85	18.9	0.21
15.00	7.64	3.20	29.5	0.35
20.00	6.40	4.10	39.0	0.50
25.00	4.80	4.70	49.5	0.68
30.00	4.70	6.10	56.5	0.83
35.00	3.40	5.70	62.6	0.98
40.40	2.90	6.00	67.4	1.12
45.00	3.00	7.50	71.4	1.25
50.00	2.90	8.30	74.2	1.36
60.00	2.00	8.80	81.5	1.69
75.00	1.60	10.25	86.5	2.00

TABLE XLIII

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC B AT 31.7° AFTER AZEOTROPIC DISTILLATION

Time Minutes	Area		% Conversion	$\ln \frac{a}{a-x}$
	Monomer	Polymer		
7.0	9.60	1.70	15.0	0.16
11.0	7.30	2.80	27.7	0.32
16.0	6.70	5.10	43.2	0.57
20.0	7.00	8.10	53.6	0.77
25.0	4.50	8.10	64.0	1.02
30.0	3.30	8.20	71.3	1.25
35.0	2.40	7.90	76.6	1.45
40.0	2.70	9.70	78.5	1.53
45.0	2.00	12.60	86.3	1.98

TABLE XLIV

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC B AT 40°

Time Minutes	Area		% Conversion	$\ln \frac{a}{a-x}$
	Monomer	Polymer		
5.0	8.30	1.6	16.2	0.18
10.0	7.20	3.2	30.8	0.37
15.0	5.30	4.1	43.6	0.57
20.0	5.10	6.2	54.9	0.80
25.0	3.60	6.2	63.3	1.00
30.0	2.50	6.7	72.8	1.30

TABLE XLV

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC C AT 20°

Time Minutes	Area		% Conversion	$\ln \frac{a}{a-x}$
	Monomer	Polymer		
15.0	11.40	1.10	8.8	0.09
22.5	10.60	2.80	20.9	0.24
30.0	6.50	3.50	35.0	0.43
40.0	4.90	5.70	53.8	0.77
50.0	3.60	7.40	67.3	1.12
60.0	4.00	10.40	72.2	1.28
75.0	2.20	11.30	83.7	1.81
90.0	1.50	12.20	89.1	2.22

TABLE XLVI

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC C AT 31.7°

Time Minutes	Area		% Conversion	$\ln \frac{a}{a-x}$
	Monomer	Polymer		
5.0	11.40	0.60	5.0	0.05
7.5	8.00	1.90	19.2	0.21
10.2	8.30	4.10	33.1	0.40
12.5	5.70	3.90	40.6	0.52
15.0	5.90	6.20	51.2	0.72
17.5	4.70	6.90	59.5	0.90
20.0	3.80	7.80	67.2	1.12
22.5	3.10	8.50	73.3	1.32
25.0	2.85	9.40	76.7	1.46
28.0	1.90	8.90	82.4	1.74
30.0	1.75	9.70	84.7	1.88
35.0	1.00	8.30	89.3	2.24
40.0	0.95	11.00	92.1	2.54

TABLE XLVII

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC C AT 40°

Time Minutes	Area		% Conversion	$\ln \frac{a}{a-x}$
	Monomer	Polymer		
5.0	9.50	1.20	11.2	0.12
10.0	6.55	5.00	43.3	0.57
12.5	5.65	7.40	56.7	0.84
15.0	3.80	8.50	69.1	1.17
20.0	2.00	9.30	82.3	1.73
25.0	1.60	11.50	87.8	2.10
30.0	0.95	11.65	93.2	2.69

TABLE XLVIII

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC D AT 31.7°

Time Minutes	Area		% Conversion	$\ln \frac{a}{a-x}$
	Monomer	Polymer		
15.0	8.20	0.10	1.2	0.01
30.0	9.40	0.15	1.6	0.02
60.0	8.90	0.60	6.3	0.07
75.0	8.10	0.65	7.4	0.08
98.0	7.20	0.75	9.4	0.10
120.0	11.90	1.50	11.2	0.12
135.0	10.60	1.50	12.4	0.13
150.0	11.10	1.75	13.6	0.15
180.0	10.20	1.95	16.0	0.17
240.0	10.50	2.50	19.2	0.21
420.0	9.40	4.00	29.9	0.36
470.0	8.80	4.00	31.3	0.38
537.0	6.10	3.50	36.5	0.46
670.0	7.30	4.80	39.5	0.51
800.0	6.20	4.40	41.5	0.54
967.0	5.10	4.40	46.3	0.62
1433.0	5.20	6.40	55.2	0.80
1635.0	4.80	6.30	56.8	0.84
1866.0	4.10	6.30	60.6	0.93
2136.0	3.70	6.50	63.7	1.01

TABLE XLIX

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC D AT 31.7° AFTER AZEOTROPIC DISTILLATION

Time Minutes	Area		% Conversion	$\ln \frac{a}{a-x}$
	Monomer	Polymer		
10.0	8.00	0.20	2.4	0.02
30.0	7.60	0.40	5.0	0.05
40.0	11.30	0.90	7.4	0.08
70.0	6.10	1.00	14.1	0.15
95.0	5.00	1.80	26.5	0.31
110.0	4.95	2.20	30.8	0.36
125.0	8.30	4.90	37.1	0.47
140.0	7.40	6.00	44.7	0.59
150.0	8.40	7.20	46.2	0.62
158.0	3.50	3.40	49.3	0.68
175.0	4.00	4.20	51.2	0.72
180.0	4.00	4.60	53.5	0.77
196.0	3.20	4.20	58.4	0.88
220.0	3.20	4.90	60.5	0.93
235.0	2.80	4.80	63.2	1.00
247.0	2.40	4.90	67.0	1.12
267.0	2.60	6.40	71.1	1.24
281.0	2.10	5.20	71.3	1.24
293.0	2.20	5.90	72.8	1.31
309.0	2.00	6.10	75.3	1.40
322.0	1.65	5.20	76.0	1.44
338.0	1.65	6.00	78.4	1.53
363.0	1.45	6.10	80.7	1.65
380.0	1.30	6.40	83.1	1.78
420.0	1.15	6.30	84.6	1.87
516.0	1.05	8.75	89.3	2.22
600.0	0.60	7.00	92.1	2.54

TABLE L

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC E AT 20°

Time Minutes	Area		% Conversion	$\ln \frac{a}{a-x}$
	Monomer	Polymer		
60.0	6.00	0.70	10.4	0.11
105.0	6.30	1.20	16.0	0.17
150.0	5.70	2.40	29.6	0.35
195.0	4.65	3.95	45.3	0.60
242.7	3.80	4.50	54.2	0.78
308.3	2.85	5.00	63.7	1.01
365.0	2.45	7.00	74.1	1.35
420.0	1.50	6.90	82.1	1.72
480.0	1.20	7.90	86.8	2.03

TABLE LI

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC E AT 31.7°

Time Minutes	Area		% Conversion	$\ln \frac{a}{a-x}$
	Monomer	Polymer		
15.0	8.00	0.25	3.0	0.03
30.0	7.40	0.75	9.2	0.10
40.0	7.50	1.60	17.6	0.19
50.0	6.40	2.25	26.0	0.30
60.0	6.70	3.30	33.0	0.40
70.0	5.70	3.90	40.6	0.52
80.0	4.60	4.25	48.0	0.65
90.0	4.00	4.75	54.3	0.78
100.0	3.55	5.20	59.4	0.90
110.0	3.10	5.40	63.5	1.01
120.0	2.95	6.40	68.5	1.16
135.0	2.40	6.60	73.3	1.32
150.0	2.00	7.20	78.3	1.53
165.5	1.40	6.70	82.7	1.75
180.0	1.30	7.60	85.4	1.92
195.0	0.90	6.90	88.5	2.16

TABLE LII

CONVERSION DATA FOR THE POLYMERIZATION OF CYCLIC E AT 40°

Time Minutes	Area		% Conversion	$\ln \frac{a}{a-x}$
	Monomer	Polymer		
15.0	8.85	0.85	8.8	0.09
25.0	8.50	1.40	14.1	0.15
35.0	7.50	2.60	25.7	0.30
45.0	6.20	3.60	36.7	0.46
60.0	4.60	5.20	53.1	0.76
75.0	4.00	6.70	62.6	0.98
90.0	3.00	7.20	70.6	1.22
105.0	2.40	8.10	77.1	1.47
120.0	1.70	8.30	83.0	1.77

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